JUNE 1970

# ENVIRONMENTAL Science & Technology

**Pesticides and estuaries 478**

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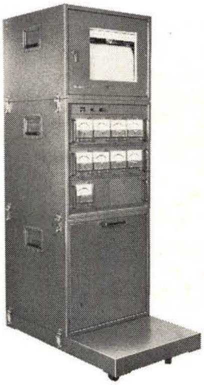

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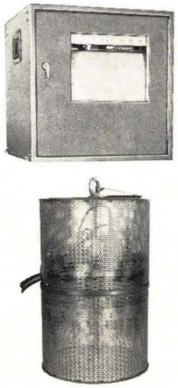

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Science & Technology

Volume 4, Number 6
June 1970

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# contents

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**Spectrophotometric determination of atmospheric fluorides 487**

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**On the significance of metal complexing agents in secondary sewage effluents 520**

**M. E. Bender, W. R. Matson, and R. A. Jordan**

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### Wastes from membrane processes

DEAR SIR:

The article by Jacob I. Bregman, "Membrane processes gain favor for water reuse," ES&T, April 1970, page 296, describes most of the favorable applications of reverse osmosis and related membrane techniques for separating purified water from contaminants. Unfortunately, it fails to state that the contaminants are discarded along with a substantial fraction of the water. A conventional aim is 90% water recovery which means that the contaminants are concentrated up to tenfold. Disposal of this waste stream is an important part of the problem which has been totally neglected by most workers.

Consider the case of salt removal from a waste stream containing initially 1500 mg./l. total dissolved solids (TDS) and producing 90% of a product stream containing 500 mg./l. TDS. The waste stream will contain 10,500 mg./l. TDS and each pound of salt carries with it 95 pounds of water. The cost of moving this much water to the ocean where it could safely be disposed of depends, of course, on the location of the plant and will obviously be highest in the interior parts of the country. Disposal in deep wells is applicable only where the local geology is particularly favorable and should not be looked upon as a general solution. Even disposal to the ocean requires enough treatment to ensure that the wastes will not interfere with the ecology of the near-shore environment. Discharge of brines to local surface waters will rarely be permitted. If organic wastes such as primary effluents are treated by reverse osmosis, it is still necessary to remove the organic matter and nutrient salts from a concentrated stream by processes which have not yet been developed.

**Robert B. Dean**
*Ultimate Disposal Research Program*
*Federal Water Quality Administration*
*Cincinnati, Ohio 45226*

### Air pollution sources reevaluated

DEAR SIR:

The determination of the sources of air pollutants precedes, logically, efforts to eliminate air pollution. As an expediency, the accounting often has been on a mass basis with particular classes of sources identified by the mass of pollutants emitted per year or day. Although the distribution among different pollutant species usually has been stated, the practice has been to sum the pollutant masses to arrive at a grand total for the purpose of comparing the contributions of different air pollution sources.

The estimates of air pollution due to various sources on such a basis are now generally well accepted. The numbers cited most often are the 1965 figures published by the Department of Health, Education, and Welfare. Similar distributions among sources can be arrived at for particular localities from more recent data. The distri-

*(Continued on page 454)*

bution among sources varies greatly from one location to another. This reflects both basic geographical differences (little space heating in California) and the results of controls already applied (absence of refuse incineration in Los Angeles).

Unfortunately, all of these distributions fail to consider that the different sources produce pollutants with different distributions among the commonly identified species: particulates, organics, oxides of sulfur, oxides of nitrogen, and carbon monoxide. Additionally, and most significantly, these chemical species vary greatly in their severity as air pollutants. For example, on an equal mass basis, sulfur dioxide is a much more severe air pollutant than is carbon monoxide.

The most objective manner in which to report air pollutant emissions would be always to list the amount of each chemical species. This, however, tends to mask the identity of a major contributor to the total air pollution because the common reader, or the expert for that matter, may find it difficult to recall whether a ton of particulate or a ton of sulfur dioxide is the worse.

A crude, but useful, approach to assessing relative weights of the several air pollutants derives from recently adopted air quality criteria. If one is to accept these criteria as setting the quality of the atmosphere in a reasonable and thoughtful manner, the appropriate weighting of each species to account for its severity as an air pollutant should be inversely proportional to its air quality level. That is, the higher the acceptable concentration in the air, the lower its danger as an air pollutant. We have calculated weighting factors for certain pollutants based on California air quality criteria. Although the weighting factors for specific compounds are readily found, the weighting factors for hydrocarbons and nitrogen oxides require some additional justification since there are no air quality standards for these compounds. There is an air quality standard of 0.25 p.p.m. for nitrogen dioxide and an air quality standard of 0.1 p.p.m. for oxidant. We used the $NO_2$ standard of 0.25 p.p.m. to calculate the weighting factor for both nitrogen oxides and hydrocarbons (mol. wt. = 86). This appears to be consistent with the levels of these compounds capable of producing 0.1 p.p.m. of oxidant. No distinction between reactive and nonreactive hydrocarbons was made as such data are available only for the Los Angeles area. It should be acknowledged at this point that air quality criteria are not held by all observers to have been arrived at in a reasonable and thoughtful manner.

The next and final step is to apply the weighting factors. Based on the distributions of emissions from particular sources among species and the weighting factors, one can make an assignment of the sources of air pollution. These new distributions of air pollution sources on an air quality basis are compared with those on a mass basis in the table below.

Distributions of Air Pollution Sources in U.S., 1965

| Source | Mass basis (%) | Air quality basis (%) |
|---|---|---|
| Motor vehicles | 61 | 12 |
| Industry | 16 | 37 |
| Power plants | 14 | 36 |
| Space heating | 6 | 10 |
| Refuse disposal | 3 | 5 |

This new assessment produces some interesting consequences. The apparent dominant role of the automobile in air pollution results from its large emission of carbon monoxide which on a mass for mass basis is the least noxious of the air pollutants. According to these methods, the relative importance on a nationwide average of automotive controls is decreased. When we apply the weighting factors to Los Angeles data we see, however, that the automobile still remains the major problem there, although its share is reduced from 88 to 50%. Industrial and power plant sources of air pollution are much more important than commonly acknowledged. A Southern California Edison Co. statement that only 1% of the Los Angeles area air pollution comes from power plants is grossly understated. Likewise, we have calculated that San Francisco Bay area industries contribute almost 50% of the air pollution in the area, and not 11% as recently proclaimed in a public statement.

We do not intend these calculations as a criticism of the current effort in control of automotive emissions. Clearly this effort is required, especially in areas like Los Angeles where the accounting system proposed here still indicates that the automobile is the major source of air pollution. (If the weighting factors took hydrocarbon reactivity data, available for Los Angeles, into account, the automobile's share would increase. Although cars contribute 68% of the total hydrocarbons, they contribute 86% of the reactive hydrocarbons.) Rather, we feel that it is important to point out that the simple statistics commonly used do not really present a true picture of the problem of air pollution.

The methods used here to assign the responsibility for air pollution certainly are not the final answer to this delicate problem. The uncertainties in the weighting factors remain high. The methods do go beyond the common approach of accounting simply on a mass basis to add a consideration of distributions among the various air pollution species and the relative severity of these species as air pollutants.

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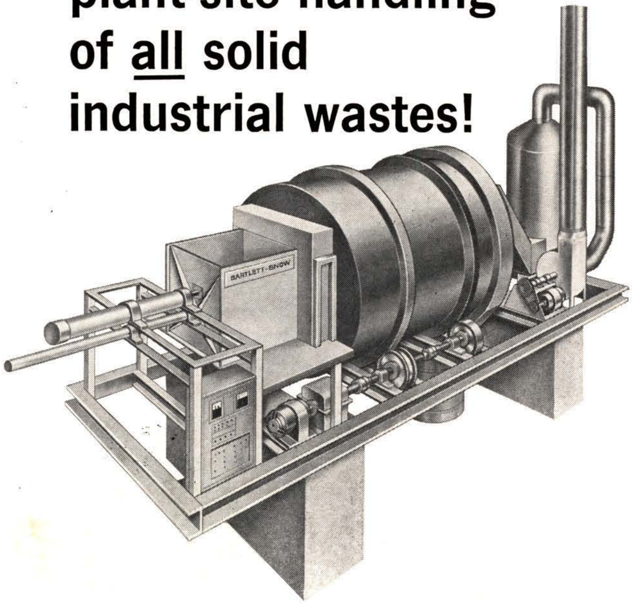

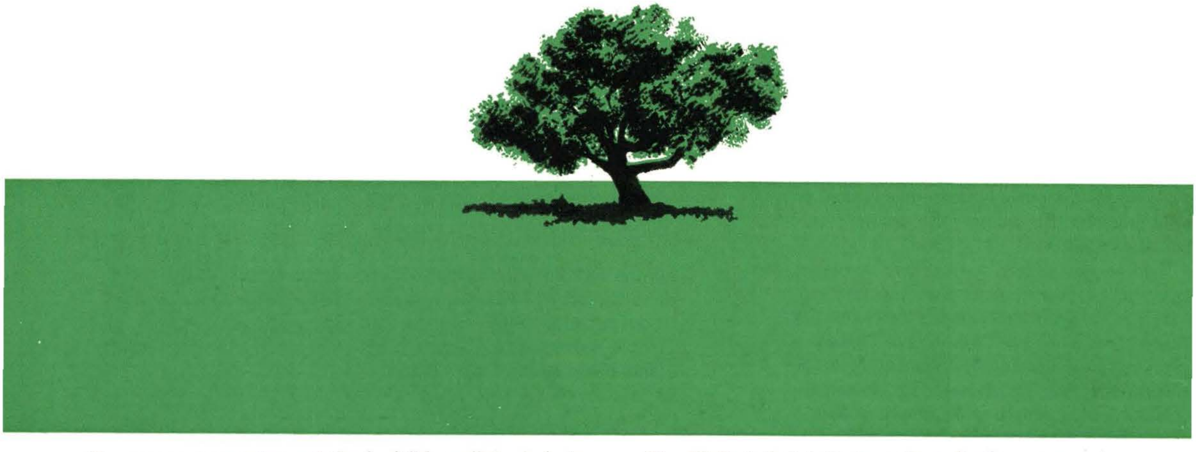

# Environmental concerns are here to stay

When environment fad is over, a hard core will still be devoted to fighting the polluter

When the April 22 Environmental Teach-In activities drew to a close, many industrialists sighed a mighty sigh of relief that a trying time had come to an end. The last automobile had been ritually buried, the last demonstrators had left the plant gates, the last TV, radio, and press stories on citizen action had boomed forth to inundate the public. Some in industry were openly gleeful that they had come through a period of intense public scrutiny with just a few flesh wounds. How fortunate, they said, that E-Day activities had been artfully transmuted from potentially damaging jugular vein attacks on industrial pollution into a harmless frolic in the sun to the pulsating beat of rock music.

We have news for those who believe that industry is now immune from attack from without. The battle has barely begun. Although many of those who were "active" on April 22 have assuredly passed on to another fad, there exists nevertheless a hard core of people who are not only concerned about the quality of the environment—they are in deadly interest when they say that they intend to do something about it. For these people, Earth Day merely crystallized previously unformed beliefs that pollution of the environment is a threat to the continued existence of our planet. One does not have to share these beliefs to be struck by the fervor with which they are held. Concern is so strong, indeed, that it would be a brave man who would predict (as some have) that in a year or so, all the fuss will be over.

To do that would be to underestimate seriously the intelligence and sincerity of those who are most concerned. They do not merely complain petulantly that youth is being left out of the decision-making processes of society (though, to be sure, that is one of the more persistent complaints). The citizen movement for a cleaner environment is, indeed, composed predominantly of young people, but they are by no means all students, or indigents, or self-seekers, or riders on a buoyant crest of youthful exuberance. Few of these people advocate overthrowing society by force. Most believe—if perhaps somewhat hesitantly—that reform and control of pollution can be achieved through the orderly processes of democracy. They certainly intend to try.

This month's Viewpoint (page 461) presents the views of Denis Hayes, National Coordinator for Environmental Action, Inc., the organization which served as the coordinating medium for the April 22 teach-in. Mr. Hayes' views are worthy of close attention from the industrial community. For Hayes promises that citizen action in the wake of Earth Day will be no fun-filled rock concert embellished by a few speeches. It will take the form of a concerted, informed effort to make industrial polluters clean up. The very legality of the steps Hayes proposes should help industry recognize that he is in earnest.

While ES&T does not, of course, necessarily endorse or reject the plans of Environmental Action, we do feel that the very existence of a strong voice in the public interest is an important part of the democratic process through which compromise decisions regarding the direction of society are always reached. To us, dangers surrounding the citizen movement are twofold: one, that industry will use its considerable powers to kill the movement when it becomes—as it will—a severe irritant; two, that the movement itself will fizzle out when it fails—as it will—to make measurable progress straight away.

Whether or not citizen concern about the environment continues to be a fairly unified, organized effort, one thing is certain—it will not just disappear. Anyone who believes that it will is in for a rude shock. The natives are restless, and it is going to take more than the usual public relations effort to pacify them.

D. H. Michael Bowen

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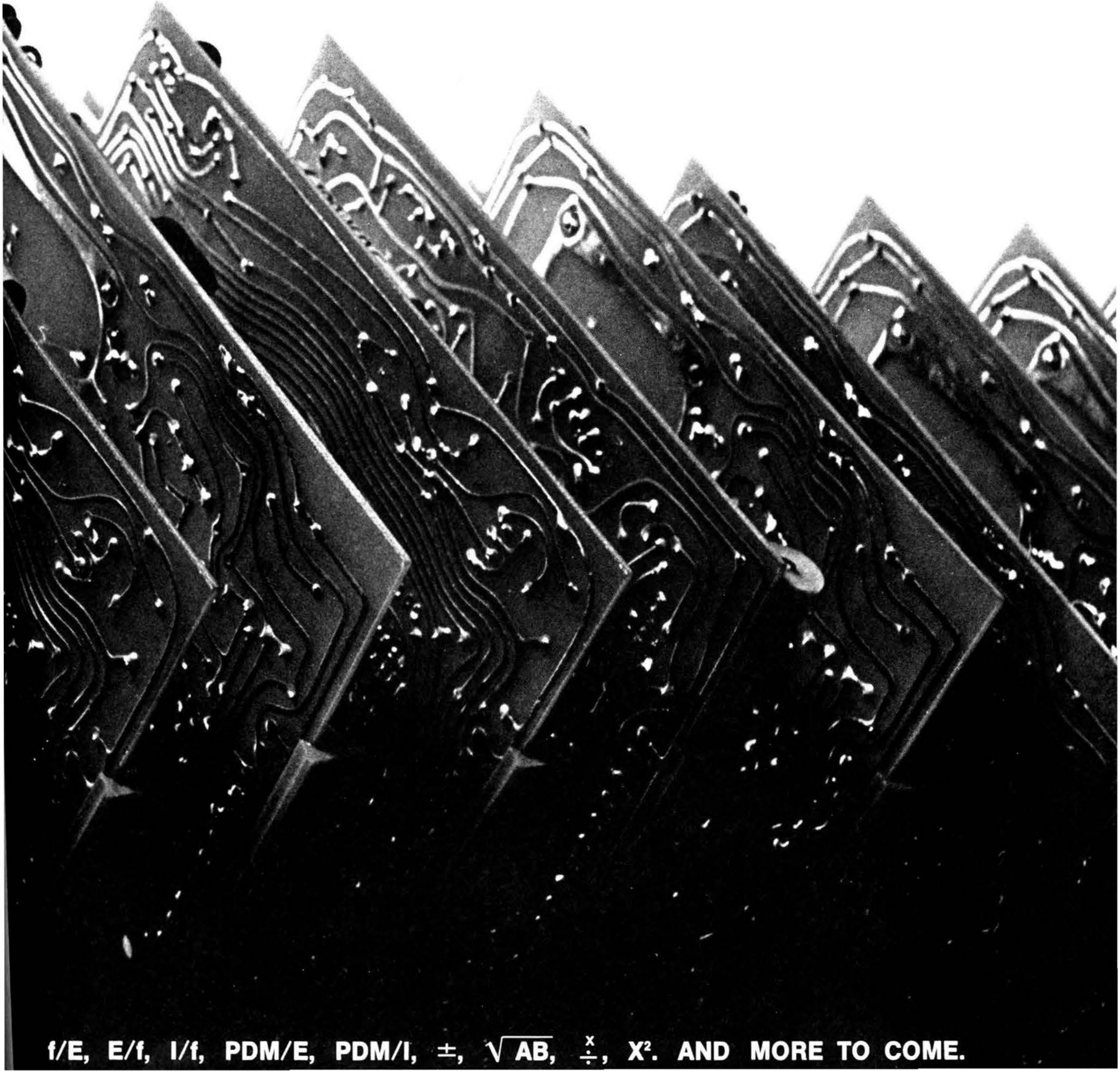

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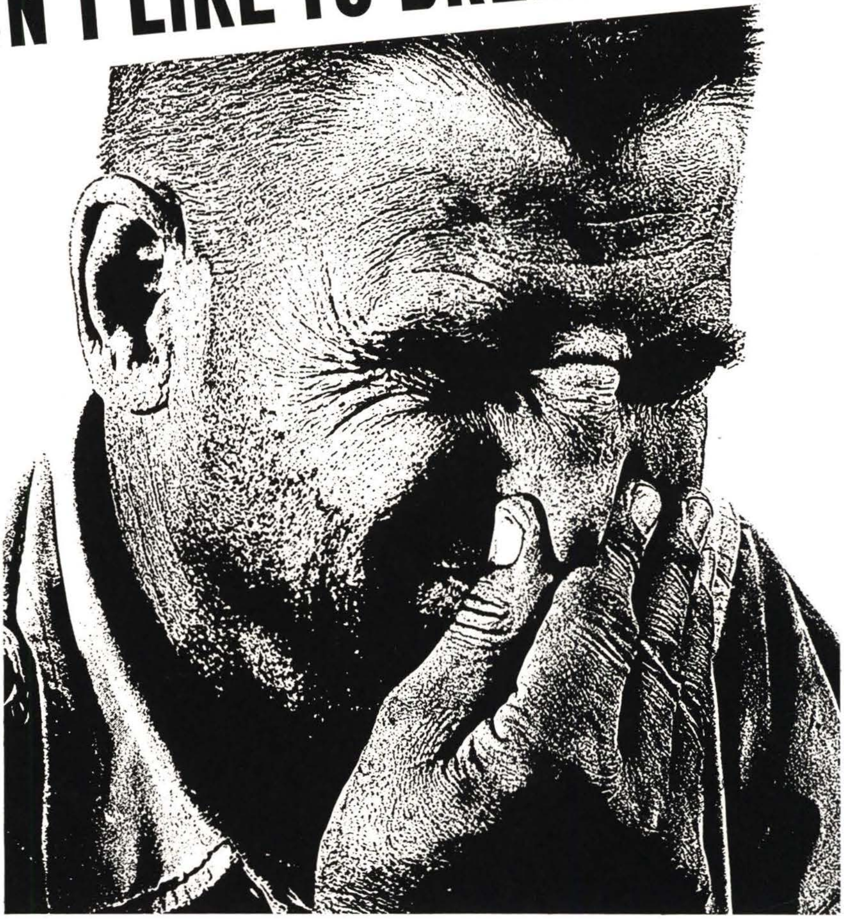

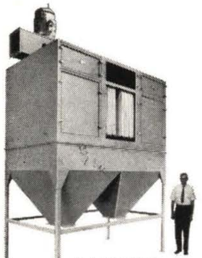

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viewpoint

Denis Hayes
*National Coordinator, Environmental Action*

# Earth Day was just the beginning

Less than four months ago, a handful of young people came to Washington and opened an office to organize Earth Day—a day of action for the environment. This effort touched a responsive chord across the country, and a movement has been galvanized.

This movement transcends traditional political boundaries. It is a movement of working men, who are breathing poison every day in the mines and mills, and who raise their children downwind of smoke-belching factories. It is a movement of people from ghettos and barrios—the worst of this country's eco-catastrophes. It includes suburbanites, who have come to realize that the effects of environmental irresponsibility do not stop at the city limits. It is the movement of a generation that has determined to make this country a place we can live in thirty years from now.

We have learned not to place our faith in the regulatory agencies that are supposed to act in the public interest. We have learned not to believe the advertising that sells us useless products. We have learned not to trust politicians who will promise the voter anything on the eve of election, but who spend the next four years raising taxes for unwanted wars, useless weaponry, moondust, and technological boondoggles like the SST—while ignoring the desperate needs of the people.

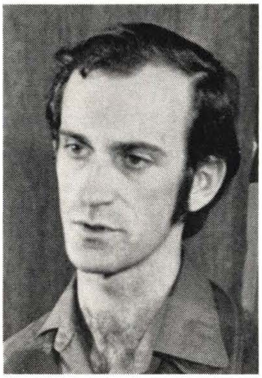
We will not appeal any more to the conscience of institutions because institutions have no conscience. If we want them to do what is right—we must make them do what is right. That will not be easy.

The following are some of the tactics we will employ:

- Stock proxy fights. Across the country, citizens are going into stockholders meetings to demand that corporations begin to put people's lives ahead of profits. They are not asking for concessions on isolated issues; they are insisting that the public interest be permanently represented on decision-making boards.
- Law suits. The courts stopped the Alaska pipeline. Companies that do not respect people's right to a decent environment, and governmental agencies that fail in their duty to protect the public interest, can expect to be sued.
- Demonstrations. In Charleston, W.Va.; Blair, Neb.; Redwood City, Calif., and scores of other communities, people confronted industries directly for the first time on Earth Day. We have found that there often is simply no other way of jolting a company into socially responsible behavior.
- Research. This organization and many local groups will be conducting investigations of corporations and of government agencies at the local and state level, similar to those that Ralph Nader's "raiders" have conducted at the federal level. There will be a vigorous effort to single out the worst offenders and to provide alternatives that are socially responsible.
- Elections. The environmental movement is going to be a powerful force in the politics of this country for the foreseeable future. Many local groups have told us they plan to join forces in statewide and regional organizations that will endorse and oppose specific candidates in the 1970 elections. Some people in this movement regard electoral politics as irrelevant; but the majority seems to feel that with so few ways of bringing about real change, we cannot afford to abandon the political arena to two calcified parties.

There is an unease across the country today. People know something is wrong. The war is part of it, but the more thoughtful critics of the war have long known that the war was just a symptom of something much deeper.

A lot of strategies have been used in the past by people seeking change. Movements have come and gone. In some very real sense, this movement may be our last chance. Our very survival demands that a new constituency be built—of people who will affirm the enhancement of life over the culture of death. Earth Day was a beginning.



*Denis Hayes, a 1969 graduate of Stanford University, studied government at Harvard before leaving to join Environmental Action in January 1970*

**WASHINGTON**

## NAPCA announces emissions report and new contracts

Adoption and enforcement of appropriate emissions limitations for major stationary sources of air pollution, regardless of where they are located, are vital steps in the nation's attack on air pollution, according to a Department of Health, Education, and Welfare report, which was required by the Air Quality Act of 1967. The report findings are essentially an endorsement of the administration's legislative proposal S. 3466 (ES&T, May 1970, page 378). The National Air Pollution Control Administration (NAPCA) recently announced three contracts with the National Academy of Sciences. The studies will: • Assess the effects of lead, fluorides, and polynuclear organic matter for criteria documents which are expected next year. • Report on noxious pollutants from federal facilities. • Review R&D $SO_2$ control technology.

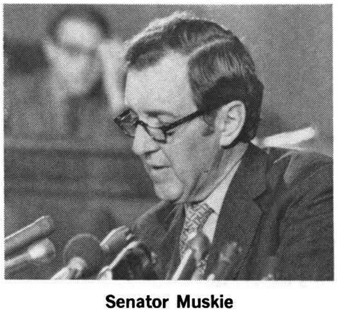
## FWQA updates its cost of clean water estimate

In its third annual updating, the Federal Water Quality Administration (FWQA) finds that the Nation is faced with the following expenditures for water quality enhancement: municipal treatments works ($9.9 billion); sanitary sewer construction ($6.2 billion); industrial investments ($3.3 billion); installation of industrial cooling facilities ($1.9 billion); and industrial operating and maintenance costs ($5.3-5.7 billion). Other cost estimates include: collection sewers ($1.2 billion per year); sediment and acid mine drainage control ($1.7-6.6 billion); treatment facilities for federal agencies ($250 million). The report endorses the concept of user chargers and makes note of the fact that the majority of earlier grants went to small communities rather than large cities.

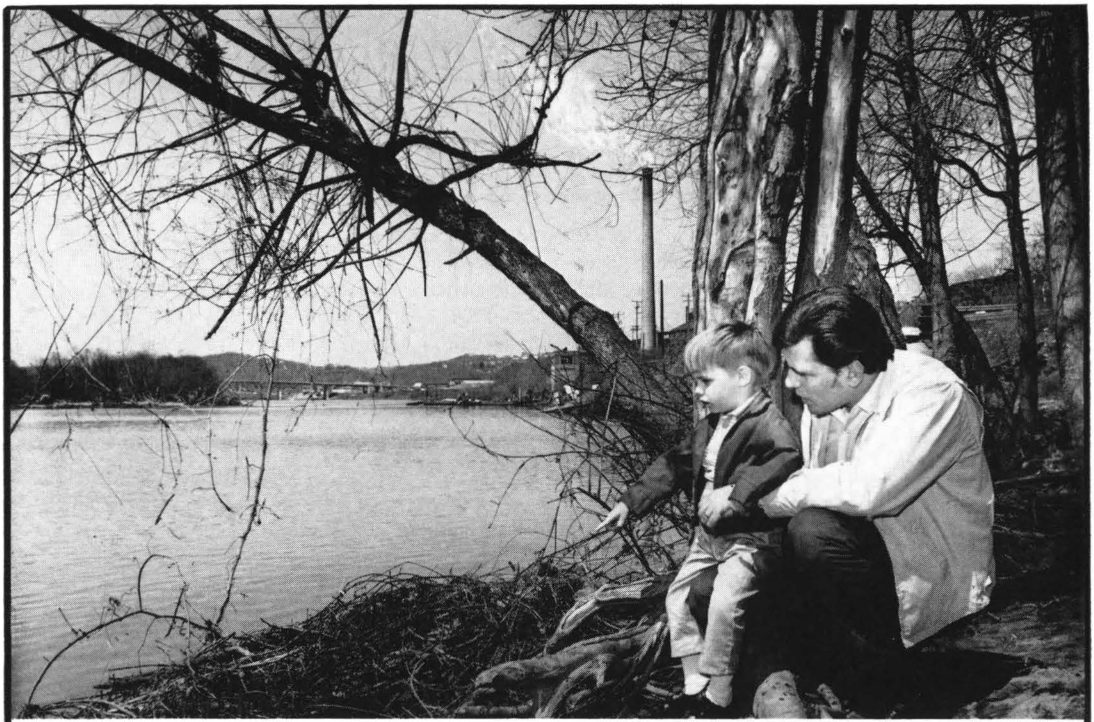
## Transportation and Agriculture comment on noise

The Department of Transportation has awarded a $327,000 contract to the National Bureau of Standards for an 18-month study on highways, and in particular tire noises. "The results of this research effort will provide a scientific basis for designing quieter tires," says Transportation Secretary John A. Volpe. Highway noise can also be reduced by barriers of trees and shrubs, according to University of Nebraska's David I. Cook and Forest Service's David F. Van Haverbeke. For maximum effects, the scientists recommend: • A distance of 75 feet or more should be placed between the source and the area to be protected. • The barrier effect is greater with tall trees spread over a large area.

## More comments on air pollution legislation


Senator Muskie

Ralph Nader's Task Force on Air Pollution released its report last month and touched off a flurry of comments on shortcomings of the present Air Quality Act of 1967. The central issue in that legislation was the different approaches to achieve air quality, namely whether to proceed with national emission standards or to proceed with ambient air quality standards with regional participation. The '67 act followed the latter approach. "There is, to this day, disagreement between knowledgeable people who agree on the objective of clean air, as to which would be the most effective approach," said Sen. Edmund Muskie (D.-Me.), at a news conference last month. Now, amendments for the '67 act are being considered in markup session and may be reported soon.



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# environmental currents

## STATES

### Philadelphia wins 42 air pollution convictions

First quarter 1970 convictions for violation of the city's Air Management Code and Regulations totaled 42, according to Edward F. Wilson, Assistant Health Commissioner for Air Management Services. Most of the violations were for the creation of smoke and fumes, involved first and second violations, and resulted in fines of $2750. Third and subsequent convictions for individual companies carry a mandatory fine of $300.

"The George Sall Metals Co., among the city's major air pollution problems, was convicted on 15 violations for excessive odor and fume emissions," says William Reilly, director of Philadelphia's compliance and enforcement division. Two other cases were discharged; two are continuing, and four others are pending other investigations.

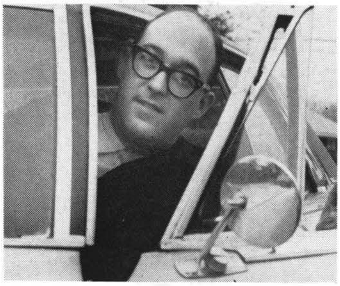
### Colorado upgrades its water quality standard

Following a recent round of public hearings, the Colorado Water Pollution Control Commission has now come to grips with some key upgrading of its water quality standard. "Final approval of these actions by the commission is likely this month," says Fred W. Matter, supervisor of the water pollution control division in the Colorado Department of Health. "Then, they will be submitted to the Federal Water Quality Administration."

The changes include: • Change in the language of the nondegradation clause; the earlier language was not acceptable to the federal government.
• Upgrading of water usage for the Platte River which flows through Denver.
• Upgrading of certain stretches of Colorado water from B-2 classification (warm water fishery) to B-1 classification (cold water fishery).
• Specification of bacteria content for class A (withdrawn for domestic use), B-1, and B-2 waters, and temperature limits for B-1 and B-2 waters.

### New York designates commission for air standard

The Interstate Sanitation Commission has been designated the coordinating and planning agency for New York City's air quality control region, which involves three states—New York, New Jersey, and Connecticut. Natale Colosi, chairman of the commission, notes that it will:
• Assist in the development of comparable standards for air quality within the region. • Work with the states in improving the coordinated actions taken during stagnant air periods and times of pollution episodes.
• Coordinate plans and strategies for the prevention and control of air pollution within the region. In another New York action, asbestos spraying of materials must now meet ten precautionary measures which were spelled out in the New York City Air Pollution Code, according to Robert N. Rickles, new commissioner of that city's Environmental Protection Administration.


Commissioner Rickles

### States receive federal help on water facilities

Wisconsin, South Carolina, and Oregon have each received grants totaling more than $1 million each from the Federal Water Quality Administration (FWQA) for construction of waste water treatment facilities.

These grants are a part of FWQA's program to build $74 million worth of waste treatment facilities in 54 cities and communities. With its eight federal grants totaling near $2 million, Wisconsin plans facilities in five cities and three villages, according to its Department of Natural Resources.

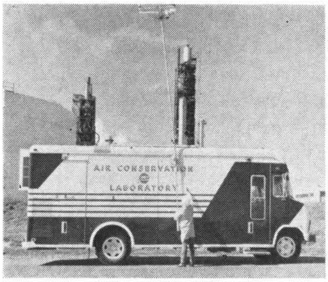
**TECHNOLOGY**

## Carbon adsorption process patented

Calgon Corp. has been issued a patent on clarification/adsorption waste water treatment. The process as covered by U.S. Patent 3,455,820 "comprises treating raw sewage with a flocculant to cause separation of solids from the liquid, separating the effluent from the flocculated solids, passing the effluent through at least one bed of activated carbon, and periodically backwashing and regenerating the activated carbon." The patent covers either organic or inorganic flocculants, and states that the solids content of the clarified sewage must be below 100 p.p.m. for efficient operation of the carbon. Inventors of the process, D. G. Hager and R. S. Joyce, state that granular carbon of minimum mesh size of 50 is preferred to prevent losses during regeneration. The process is already being used for municipal and industrial treatment (ES&T, April 1969, p. 314; Sept. 1969, p. 809).

## Desalination by geothermal energy

Geothermal energy may be useful for low cost desalination, according to Prof. A. K. D. Laird of the University of California, Berkeley. Laird, who has received a grant from the Office of Saline Water, to study the concept, says the billion acre-feet of 600°–800° F. brines that underlay California's Imperial Valley contain enough energy to convert brackish water to freshwater supplies for agricultural irrigation in the area, perhaps for as long as fifty years or more. Laird's study will consider capacity and possible location of geothermal wells as well as desalination process designs that might be applicable.



Gulf's monitoring van

## Gulf mobile air monitor

Gulf Oil has placed into service a mobile monitoring van, developed by its research and development subsidiary, to survey pollutant levels at its refineries and plants. The 25-foot van, operated by a two-man team, is equipped for on-the-spot detection and evaluation of seven major pollutants—ozone, hydrogen sulfide, carbon monoxide, hydrocarbons, particulates, and oxides of sulfur and nitrogen—and also to identify any units or systems where corrective action is required. A similar unit for monitoring quality of water effluents has been in routine service at Gulf installations for two years.

## Thermal discharges for fish production

An experiment in beneficial uses of thermal discharges will be conducted at TVA's Gallatin Steam Plant. Food Systems, Inc., of Nashville, Tenn., is moving in equipment for a one-year research project on commercial catfish production, a rapidly growing industry in the South. Because the fish do not feed actively in cold weather, heated water may be a way of lengthening the growing seasons for catfish fingerlings. If results are favorable, the agreement approved by TVA provides for expanding the project into a developmental study for commercial production.

# environmental currents

***INDUSTRY***

## Central waste disposal plant opens in New Jersey

John W. Rollins, Sr.

**Rollins-Purle, Inc.** (Lansdowne, Pa.), has opened the first in a planned series of waste disposal facilities in Logan Township, N. J. The plant is located on a 212 acre site and is capable of handling 250,000 gallons of concentrated industrial waste per day. Treatment will be through a combination of biological, physical, and chemical steps (ES&T, March 1970, page 195). John W. Rollins, Sr., president of **Rollins International, Inc.** (Wilmington, Del.), parent company of Rollins-Purle, reiterated at the plant opening his previous prediction that the firm will construct 75 to 100 such plants over the next 3 to 5 years. A second plant in Baton Rouge, La., is scheduled for start-up in July.

## Foxboro sees business in environmental control

Ralph Hayden, Jr., president of the **Foxboro Co.** (Foxboro, Mass.), told stockholders at their annual meeting that he believes recent concern of the public with environmental quality offers promising business opportunities for his company in the 1970's. Hayden explained that since most Foxboro products are used in process control, the company's main contribution would be through pollution prevention, made possible by better industrial efficiency. He stressed, however, that Foxboro also expects increased sales of instruments and systems intended specifically for pollution measurement. Among these are ion selective, oxidation–reduction potential, and conductivity measurement systems.

## Business developments in the pollution control field

**Westinghouse Research Laboratories** has formed an ecological systems department to coordinate and expand technology studies affecting the environment. **Procon, Inc.** has created a waste management group to ensure that efficient pollution control systems are incorporated into old and new plant designs. A specialist team will supply pollution control know-how to each Procon project. **Pullman, Inc.** has acquired **Aloe Coal Co.,** a firm that has been providing solid waste disposal services for Pittsburgh. **Pullman Environmental Services** has also been formed to coordinate environmental control activities not already undertaken by present Pullman divisions. **Envirotech Corp.** has finalized the purchase of **Goslin-Birmingham, Inc.,** a process equipment manufacturer, from **Control Data Corp.**

***CAREERS***

## Students—Be an air pollution control inspector

A challenging job for those who want to do something constructive about cleaning up the environment is that of air pollution control inspector with the New York City Department of Air Resources. Commissioner Robert N. Rickles is urging those with a bachelor's degree plus one year's experience or with a high-school diploma plus five years' experience with air cleaning devices to apply for jobs with his department. The posts are "far more technical than merely chasing smoke," according to Rickles, and applicants who still have a military obligation may be able to obtain draft deferments. Although initial openings may be filled by press time, the department probably will have additional positions available later this year.

# FRONT FIVE

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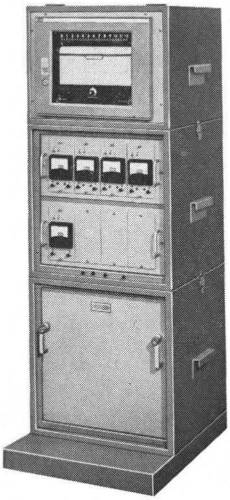

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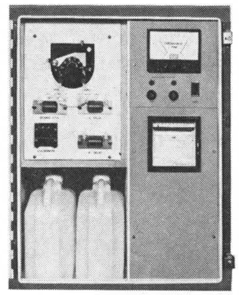

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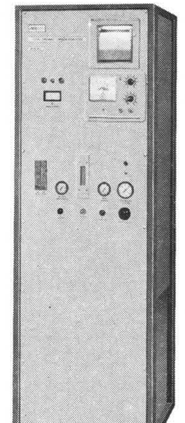

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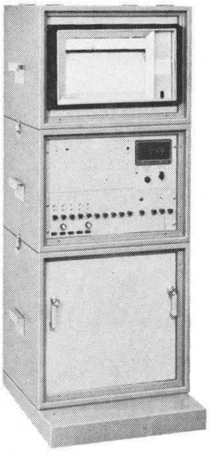

A parallel can be found between water and air quality monitoring, and the defense execution of a championship football team. Both must generate rapid, accurate determinations as a "first line of defense". Thus, the AES "front five" — a significant group of automated systems for continuous, unattended measurement of up to 30 chemical and physical parameters. Each is available in a variety of configurations— a total capability designed, engineered, installed and maintained by AES. Each may be housed in shelters, mobile vans or trailers, complete with telemetry and data acquisition. Because of their high reliability, more AES systems than others are at work at federal, state and industrial sites throughout the world. Ask about our Total Systems Lease Plan and our "guaranteed data" maintenance programs.

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*Coupled with last year's cost estimate for organics, the majority of the chemical industry's waste water treatment cost is assessed*

# Inorganic chemicals industry:

# Clean water cost estimate

"Economics of Clean Water," the third annual report to Congress on the cost of clean water for the U.S., contains waste water treatment profiles for municipalities, animal feedlot wastes, and the inorganic chemicals industry. Required by the Federal Water Pollution Control Act, this report details the in-depth cost estimates for achieving certain levels of waste water treatment within these particularly troublesome areas.

The municipal profile, Volume I, forms the basis for the administration's request for funds to provide $10 billion for construction of municipal treatment facilities between now and 1974. The animal feedlot wastes profile, Volume II, is of special concern and interest to the Council on Environmental Quality. Volume III comments on the inorganic chemicals industry. These three volumes plus a summary report complete this year's updating.

Together with last year's profile on the organic chemicals industry, the third volume now affords the cost estimate for treating the waste waters from 80–90% of the chemical industry in the U.S.

During the five-year period, 1970–1974, the inorganic chemicals industry will have to increase its outlays nearly eightfold to reach the 100% level of treatment. On the other hand, just to keep up with its present level of treatment, the industry must increase present outlays for capital and operating expenses more than 50%, from $414.5 million in 1970 to $630.2 million in 1974. Earlier, last year's estimate found that the organic chemicals industry would have to spend $234–331 million for an earlier five-year period, 1969–73.

The inorganic chemicals profile was developed under contract by four consulting engineering firms—Cyrus Wm. Rice, a division of NUS Corp. (Pittsburgh, Pa.), which served as coordinator for three other firms—Resource Engineering Associates, Inc. (Stamford, Conn.); Datagraphics, Inc. (Allison Park, Pa.); and Gurnham, Bramer, and Associates, Inc. (McMurray, Pa.). It is based on data representative of 59 inorganic chemicals plants from more than 2700 plants in the U.S.

Fred Stein, the federal project manager for Volume III, notes that this profile, as well as others, serves a number of real purposes: They

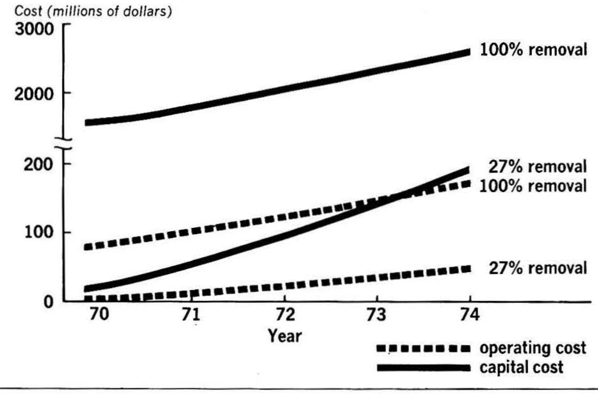
- Give the R&D people the state-of-the-art for handling specific wastes within certain trouble areas.
- Present the economic alternatives and cost curves for treatment of wastes within specific industrial segments covered by the profiles.
- Detail the manpower requirements for waste water treatment operators in this particular segment of U.S. industry.

### Treatment levels

Only costs for two levels of waste water treatment were considered, namely 27% and 100%. The 27% removal figure represents the current overall level of efficiency within the entire inorganics industry. Of course, the 100% figure represents the universal application of advanced waste treatment practices for complete pollutant removal.

Due to the fact that inorganic wastes are primarily inorganic solids that respond only to physical treat-

**Cash outlays facing the inorganic chemicals for waste water treatment, 1970-74**



Source: NUS.

ment methods, intermediate levels of removal efficiency are not distinguishable because there is no intervening technology. Unlike the case for organic waste waters (ES&T, April 1969, page 311), there is no series of technological plateaus through which the whole population may progress.

There is nothing magic about the 27% figure. Some existing plants have complete treatment facilities in operation today. Most have facilities only for neutralization and suspended solids removal. On the average, 27% of the industry's total pollution load is removed before discharge. So, the projected five-year estimate gives the cost for equipping the industry to remove the remaining 73% from existing plants in addition to that from plant expansions, new plants, and anticipated technological changes.

### Input-output

In its operation, this industry produces eight major groups of industrial materials. Although its products are used for variety of industrial purposes, the identity of products are far removed from consumer identity.

Including eight separate Standard Industrial Classification (SIC) numbers, the inorganic chemicals industry, for the purposes of the profiles, nevertheless includes:

- Alkalies and chlorine.
- Industrial gases (except organic).
- Inorganic pigments.
- Paints and allied products.
- Fertilizers (excluding ammonia and urea).
- Inorganic insecticides and herbicides.
- Explosives.
- Other major industrial inorganic chemicals.

### Wastes characteristics

Solids are the big problem in the treatment of this industry's wastes, both dissolved and suspended solids. In general, biological methods of treatment are not applicable. So, the physical treatment methods of equalization, neutralization, flocculation, sedimentation, and sludge dewatering are employed.

The industry's waste waters are either contaminated waters from process operations or relatively clean waters from cooling uses, general washings, and the like. Practically all plants practice the segregation of contaminated and clean wastes.

An estimated 40–80% of the industry's use of water goes for cooling purposes. In fact, many process facilities generate large amounts of thermal energy which must be removed either by the circulation of cooling waters or air, the profile points out. These contaminated wastes usually come from the following four areas:

- Electrolysis and crystallization brines.
- Washings from filter cakes.
- Spent alkalies and acids.
- Washings from raw materials.

Plants with small discharges such as paints and herbicides, for example, employ equalization and neutralization with total discharge to municipal systems for joint treatment. Approximately 4.2% of the discharge from the total inorganic chemicals industry is sent to municipal treatment facilities. This practice is not expected to change during the five-year time span.

In general, however, the industry has found that separate treatment has economic advantages in those cases where significant quantities of waste waters are concerned.

On the other hand, other segments do not make significant use of municipal systems due to the fact that their discharges are highly contaminated with chlorides, acidity, and specific inorganic species. This is true, for example, of the following segments: alkalies and chlorine, inorganic chemicals, fertilizers, and explosives.

Nevertheless, there is wide variation within the eight SIC categories. For example, industrial gases and the paints and allied products segments, SIC groupings 2813 and 2851, respectively, use municipal sewer systems rather extensively, 40% and 60%, respectively. But the waste waters for these segments are essentially clean.

### Cost criteria

The cost estimates were developed for four levels of flow rates, three levels of acidity, two levels of suspended solids, and three levels of total dissolved solids. However, the data from the 59 plants were not sufficiently complete in regard to effluent quality to construct any statistically significant relationship between the numbers of plants and effluent quality parameters such as acidity, suspended solids, and dissolved solids.

The total costs given in the profile are for the construction and operation of waste treatment facilities only. As such, they cannot be applied to individual plants. Nor do the estimates include costs for process changeover, restriction of plant operations, or sewer segregation. Only detailed engineering studies can provide data on particular plants.

### Manpower

The manpower—operators, maintenance, and support personnel—required by the inorganic chemicals industry to achieve the two levels of treatment ranges from a low of 1826, the industry's currently employed manpower for its waste water treatment operations, through an intermediate of 2922 personnel, the manpower required by the large plants to reach a 100% level of treatment through 1974, to a high of 9365 personnel, needed in small plants by 1974 to provide the current 27% treatment level.

In general, the number of operator and maintenance personnel range from one to five. The small and large plants which normally provide 27% level of treatment would employ one operator per plant. On the other hand, the large plant that would provide 100% removal of solids normally would employ four or five operators per plant, according to the industry profile.

### Trend

In 1969, total production in the industry was 329 billion pounds of products, the profile notes. The estimated value of shipments that year valued at more than $13.1 billion. The projected 1973 output is 456 billion pounds, valued at $16.9 billion.

Expenditures for pollution control will be of greater relative significance in the inorganics segment of the chemical industry than, for example, the organics or remaining segments of the chemical industry for a number of cogent reasons. For example, the growth rate for inorganics historically has been 1.5–2.0% of the GNP. However, in recent years, the overall price index of its products has fallen 2–5%.

Nevertheless, certain segments within inorganics will grow. For example, its industrial gases segment is expected to increase 18% during the five-year time frame. As a whole, the industry is tending to concentrate in the midwest and southwest, according to the profile, reflecting the continuing trend in this industry to locate production facilities near raw materials and markets.

# Public advisory group hears water pollution needs around U. S.

The President's Water Pollution Control Advisory Board is a group of nine presidential appointees, each with different professional backgrounds and geographical locations. The board advises the Secretary of the Interior who, in turn, ultimately advises the President on approaches to protect and enhance this nation's water environment. This advisory board meets to review pressing water pollution problems in trouble spots throughout the U.S., usually at the invitation of a governor or the Secretary of the Interior.

Its most recent meeting, actually its 49th since formation of the board in 1956 under authority of P.L. 84–660, was held at the request of board members. The problem concerned pollution of the lower Mississippi River and oil spills—more specifically, Chevron's spill in the Gulf of Mexico. Following a two-day meeting in New Orleans, the board met in the Virgin Islands.

As a result of these meetings, the advisory board passes resolutions and refers them to the higher-ups for ultimate disposition. Obviously, the board has passed many resolutions, some of which have been heeded by the higher-ups and some of which have not. However, the board's batting average seems to have improved over the past year. More importantly, the board serves as an important information source for decision-makers in Interior.

### Explanation

The board's earlier meeting (January 12–14 in Houston, Tex.) illustrates the type of resolutions passed and ultimate disposition of these items. For this meeting, Texas Governor Preston Smith invited the board to comment and review the water pollution problems associated with the Houston Ship Channel and Galveston Bay, a recreational as well as an industrial area. Its January meeting was not the first held in this area on Texas' problems. In 1967, the board considered the problems but failed to implement solutions, hence the revisit.

Following its second visit, the board passed four resolutions; the first is now a *fait accompli;* the second has been incorporated into pending legislation; and the third and fourth items necessitate more study before it can be said that they have been successfully implemented (see scorecard).

Perhaps, other experiences from the Texas meeting also illustrate the functions and operation of the board. "Our findings in Texas revealed that the city of Galveston was polluting its own beach areas by dumping raw sewage into Galveston Bay," says Gordon E. Kerr, executive secretary of the advisory board. At this meeting, chairman Carl L. Klein, Interior's assistant secretary for water quality and research, asked the Texas Water Quality Board (WQB) to take immediate corrective action, by upgrading treatment facilities. "Two weeks after the meeting, corrective action was initiated, continues today, and will be carried forth till complete upgrading is completed," says Gordon Fulcher, the Texas WQB chairman. With a new chairman and emphasis on getting permit holders in compliance, the Texas board—the one and only board responsible for water pollution control within the state—stands ready to make a renewed effort to curb Texan water pollution problems. In fact, the effort has been proceeding since last fall when Fulcher was elected chairman of the Texas board.

Of course, the 1970 problems in Texas are different from those when the board last met there in 1967. Then, no single responsible agency in the Texas legislature could be recognized, or properly and solely charged with the responsibility for water pollution abatement in the state. This is not to say the Texas Water Board was not operating in 1967. But one responsible agency was not properly identified so that the public, industry, and local governments knew to which office they should turn.

Things are different today. Now, the WQB has been singled out and is accountable and directly responsible to the public for water pollution abatement. After the January meeting, the

Carl L. Klein

"Under section nine of the Federal Water Pollution Control Act, the board advises, consults with, and makes recommendations to Interior Secretary Walter J. Hickel. I have been meeting with the board in the secretary's stead.

"The board obtains input from as many sources as possible and senses the pulse beat of future water pollution abatement developments. At times, the board has been very critical, but now the board has been coming up with new thoughts and ideas. As a result, the Department of Interior is obtaining a better input on the ways to proceed on water pollution abatement.

"The board can function well. If the individual members function well, then the board functions properly."

**Members of President's Water Pollution Control Advisory Board**

Carl L. Klein, Chairman, Interior's Assistant Secretary for Water Quality and Research
Gordon E. Kerr, Executive Secretary
Robert H. Finch, *Ex-Officio* member, Secretary of Health, Education, and Welfare

**Term expires June 30, 1970**

W. James Lopp
Security analyst

Edward P. Morgan
Television newscaster

Stephen E. Reynolds
Engineer

**Term expires June 30, 1971**

Louis S. Clapper
Conservationist

Ralph W. Kittle
Businessman

Stuart M. Long
Newspaperman

**Term expires June 30, 1972**

Melbourne R. Carriker
Oceanographer

Wallace W. Harvey
Physician

Parker E. Miller
Land developer

## Scorecard of advisory board meetings in 1970

| (Problem area, dates, and location) | Resolutions passed by board | Subsequent action by higher-ups |
|---|---|---|
| **Ocean disposal**<br>**May 1 to 2**<br>**Virgin Islands** | • Too early for final comment. | • Too early for implementation. |
| **Oil spills**<br>**April 29 to 30**<br>**New Orleans, La.** | • Too early for final comment. | • Too early for implementation. |
| **Lake eutrophication**<br>**March 2 to 3**<br>**Washington, D. C.** | • Urged board's attendance at the recent FWPCA workshop as observers. | |
| | • Commended the President on developing and initiating a broad attack on contamination of the environment. | • Included in Nixon's state of the environment message. |
| | • Urged the Secretary of Interior to support legislation which will prohibit the disposal of polluted dredging in the Great Lakes either by public or private agencies and individuals. | • Hickel's notice to Reserve Mining Co. (ES&T, April, page 270) and Nixon's message to Congress on April 15 (H. Doc. No. 91-308) prohibiting dumping in Great Lakes dredged spoils. |
| | • Urged FWPCA to investigate the current water pollution problem in the Virgin Islands. | • Board revisited the islands on May 1 to 2 to prod the local government on water pollution abatement action. |
| **Galveston Bay**<br>**January 12–14**<br>**Houston, Tex.** | • Urged spending the $800 million appropriated by Congress to be used immediately. | • Included in Nixon's state of the environment message of Feb. 10. |
| | • Urged all waste water being discharged to coastal waters to receive at least secondary treatment. | • Incorporated in proposed legislation which is pending. |
| | • Urged prohibition of deep well injection of any water that has a chance of getting into aquifiers. | • Requires more study before any action can be taken. |
| | • Urged spending more money for studies on how to remove viruses from water. Ordinary treatment does not remove them. | • Requires more study before any action can be taken. |

board and its new chairman, Gordon Fulcher, now look forward to a year of renewed activities.

### Other meetings

Many other advisory board meetings have been held in different locations throughout the U.S. In fact, the board has visited some on more than one occasion. Comments on much earlier meetings would perhaps only serve to bring out old skeletons from the federal closet.

It is not to be inferred that all actions resolved by the board are accepted without question. In some cases, the board made resolutions which were not endorsed by the higher-ups.

For example, at a May 1969 meeting in Washington, D.C., the board passed a resolution urging the financing of waste water treatment facilities. Although the resolution was adopted by the board, the resolution was not adopted by Interior's Secretary Hickel. Perhaps, the timing was premature.

### Criticism

Edward P. Morgan—a Johnson appointee, a television newcaster (Washington, D. C.), and lame duck whose term expires the end of this month—says, "The board is a joke. Under existing circumstances in the present administration, the board has become emasculated, useless, and probably should be removed." With the creation of the Council on Environmental Quality (CEQ), no one knows where this public advisory board fits in with other environmental activities.

"Present assistant secretary Klein is just not with it in the terms of an aggressive policy in terms of solving water pollution problems," Morgan says. "I speak for myself, but I also know that some other members of the board are distressed that the assistant secretary shows no more aggressiveness than bold talk.

"During 1969, the board was dormant, for all intents and purposes nonexistent," the newscaster reports, "We had difficulty trying to set up an executive meeting during the Houston trip (January 1970) to find what the board was being asked to do. Other than listening to what other board members themselves had decided to do, the new members of the board were left completely in the dark on purposes and intent of their involvement.

"The main distinction between administrations is that however ineffective the board may have been under the Johnson administration, at least I personally had the impression that we were being listened to," Morgan says. "Whether the board's resolutions were being accepted or not, I cannot say.

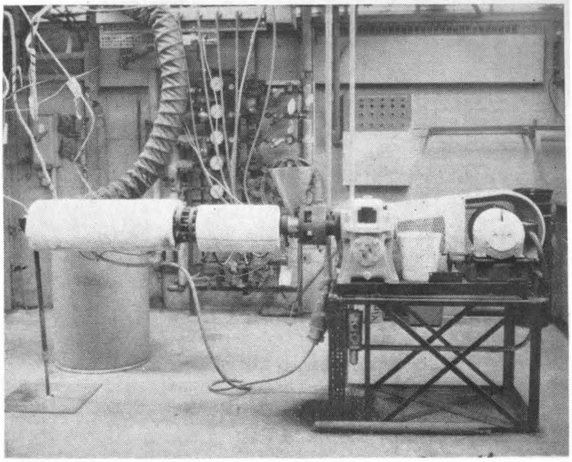
"Since then, I have had the impression and experience that the board is barely being tolerated and furthermore, that we were simply wasting the taxpayer's money, the modesty of the board's budget notwithstanding."

But all is not bleak. The board's public hearings do have a definite positive effect in the local areas. "They stir up interest which gets a flurry of attention in the media," Morgan says. "What lasting effect they have, time will tell."

The one big question still remains. "What are the function, position, and reason for being for this public advisory board in light of the newly created CEQ?" Morgan queries. So far, no clarification has been forthcoming from the higher-ups.

# Plastic wastes yield to pyrolysis

## *Technique could return troublesome waste back into raw material cycle*



**Laboratory.** *Experimental runs were on 1¼" unit; pyrolysis tube is at left. Company has also developed 100 pound per hour pyrolyzer*

Current concern over solid waste problems is bringing one often overlooked point into sharper focus: Modern technology, with its insatiable appetite for raw materials to convert into a myriad of forms and seemingly indestructible compounds, very often carries the seeds of solutions to the waste problems that result. Pyrolysis, a well developed industrial process, is getting serious consideration for upgrading a wide range of wastes. And with the recent emphasis on segregating wastes for reclamation, pyrolysis may be the way to contend with one of the problems in solid waste management, plastic waste, says J. E. Potts of Union Carbide's chemicals and plastics division.

According to Potts, in the past 15 years Carbide has developed considerable technology in pyrolysis (which differs from destructive distillation in that almost the entire pyrolyzate is recovered as a nondistillable melt) as a way to convert low cost resins, such as polyethylene, into waxes, greases, and liquids. In the course of this work, it has been shown possible to pyrolyze many plastics, including high and low density polyolefins, polyvinyl chloride, polystyrene, and their copolymers, both individually and in blends. By varying process conditions, the products obtained can be either solid, waxy materials, high viscosity liquids, or even gases; the chemical reactivity of many of these make waste plastic a possible source of chemical intermediates.

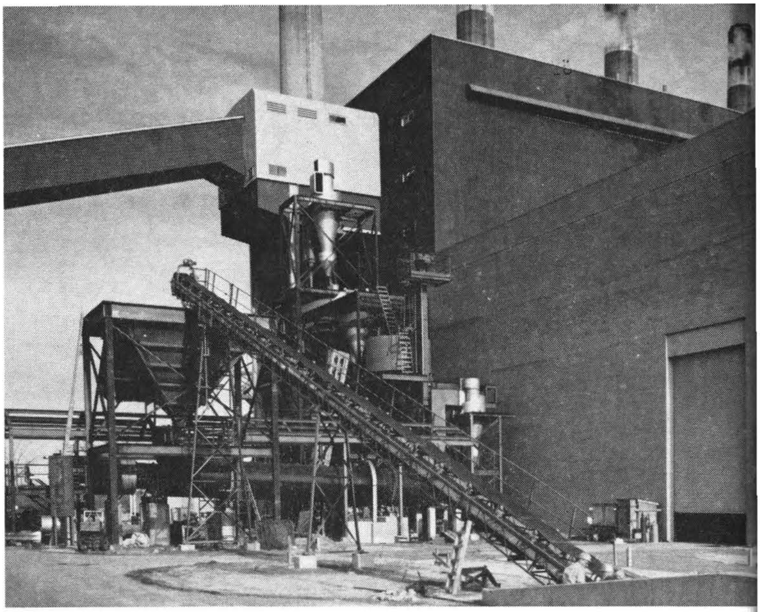
The equipment used for plastic pyrolysis consists of a conventional screw extruder fitted with a pyrolysis chamber at the discharge end. The pyrolyzer design developed by Carbide is of annular construction, in which the material is forced through a relatively narrow electrically heated annulus. After melting in the extruder and being heated to 300° C., the feed is further heated in the pyrolyzer to between 400°–600° C., a range suitable for most of the plastics studied. Because of the uniform temperature distribution obtained by the annular design and because the viscosity of the product can be used as feedback for automatic temperature control, a product quite uniform in molecular weight and viscosity can be obtained. The degree of pyrolysis, and thus the gross properties of the product, is determined by temperature and residence time in the unit.

Multicomponent plastic waste is probably the largest potential source available for pyrolysis, since separation of waste plastics by types would not be feasible. The use of mixed plastics for secondary refrabrication of finished goods is not possible, since processing techniques require materials of high purity and uniformity; in fact, almost all high grade scrap from plastics plants is already utilized. But mixed plastics offer no inherent difficulties in pyrolysis, says Potts. The wide variety of volatile compounds encountered, such as HCl from polyvinyl chloride and the various plasticizers present in some resins, can readily be handled by a venting section on the extruder. And Carbide's experimental data indicate that most hydrocarbon polymers do not vary markedly with respect to pyrolyzing conditions.

Carbide has not as yet done any application work on pyrolysis products of waste plastics. But to illustrate the potential of the concept, Potts points out that the company has developed and patented some products manufactured by the pyrolysis of polyethylene resin, among them paste waxes, polishes, printing inks, mold release agents, lubricants, textile finishing agents, and adhesives.

In chemical composition, the products of waste plastics pyrolysis are somewhat like crude petroleum, the most noteworthy difference being the absence of polynuclear aromatic hydrocarbons and a higher average molecular weight. "Because of its similarity to petroleum," Potts says, "it's conceivable that pyrolyzed plastic waste could serve as a petrochemical raw material, either as a fuel or for chemical synthesis," if the concept is applied on a large enough scale. The possible applications he envisions include such things as upgrading asphalt compositions for heavy duty service, in aqueous emulsion form as an agricultural mulch, or possibly even as a carbon source for protein synthesis by microorganisms.

# A bear market for $SO_2$ technology



**Paducah.** TVA's *Shawnee steam plant is testing dry limestone injection process*

*As standards stiffen, utilities favor low-sulfur fuels over stack gas control*

Develop a product that satisfies a specific need in the marketplace, and the world will beat a path to your door—so goes the build-a-better-mousetrap theory that is a cornerstone of U.S. industrialism. But when the product is an $SO_2$ control system for power plant boilers, the theory doesn't work that elegantly, or, at least, there are other factors at work that don't lend themselves to epigrammatic descriptions of economic theory. Consider this fact: The number of control systems that have been announced in the past few years is growing steadily, and now amounts to somewhat over one dozen. Yet, on the other hand, just last month one of ES&T's feature authors (Ehrlich, page 396) pointed out that this year more than 6000 Mw. of fossil-fueled generating capacity will be brought on-line, without any gaseous control system added or even allowed for in the design.

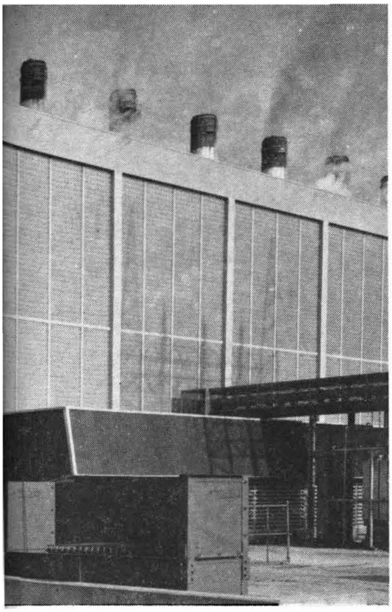
When ES&T last reviewed $SO_2$ control processes (ES&T, October 1968, page 994), the list included just over a half dozen, about half of which were said to be ready for commercialization. A brief rundown of the status of the more advanced systems includes:

- **Wellman Lord's sulfite absorption system** which has completed a nine-month demonstration run at a 25 Mw. generating unit at Baltimore Gas and Electric's Crane station. Olin Corp. has purchased a similar, but much larger, unit for one of its sulfuric acid plants in Paulsboro, N.J., and Wellman Lord has licensed two Japanese firms to market the process in Japan and other Far Eastern countries. However, no major installations on U.S. power boilers have been announced.
- **Monsanto's catalytic oxidation process** which is still operating in a pilot plant unit at Metropolitan Edison's generating station at Portland, Pa. Monsanto has incorporated commercial development of the process into its newly formed Envirochem division, but as yet none of the units have been marketed.
- **The wet limestone process** developed by Combustion Engineering which has been put on stream at two power stations. A unit at Union Electric in St. Louis, Mo., has been operating only intermittently because of mechanical problems; the other unit at Kansas Power and Light at Lawrence, Kan., has recently achieved continuous operation.
- **Dry limestone injection** which is undergoing further evaluation in a NAPCA sponsored test at the Tennessee Valley Authority's steam generating station near Paducah, Ky., which could be crucial to the future of this process. Earlier demonstrations achieved only 20–30% control of sulfur oxides, and NAPCA says that goal of the current test is to increase the efficiency to 50%.
- **The Bureau of Mines' alkalized alumina system** which has not met expectations. The future of this process is in doubt. The bureau's pilot plant has experienced formidable problems with attrition of the alumina absorbent, and before the end of the current fiscal year the bureau will have to decide whether to devote more funds to study the concept, perhaps with an alternate absorbent, or to drop the project entirely in favor of other means of attacking the $SO_2$ problem.

### Other processes

Several other stack gas control processes are under intensive development. The molten carbonate process developed by Atomics International and Princeton Chemical Research's catalytic process for reduction of sulfur oxides by hydrogen sulfide, both announced about two years ago, are still in the laboratory pilot-plant scale; the molten carbonate process, however, is said to be ready for testing on a continuous basis. And developers of the alkaline absorption/electrolytic regeneration processes, Stone and Webster and Ionics, Inc. are looking for funds to support a demonstration project. The companies have been issued patents on the process, and NAPCA is currently funding a study on optimizing absorption units for the system.

Among the more recent entrants in



to the $SO_2$ control field is the magnesium oxide absorption process developed jointly by Chemical Construction Corp. and Basic, Inc., which features a central sulfur recovery plant approach. Sulfur oxides are removed from the flue gas by magnesium oxide, and the resultant magnesium sulfate is scrubbed from the stack gas along with the fly ash in a wet venturi scrubber. The spent absorbent can be shipped to a central unit, which may serve several power stations or chemical plants, for recovery of sulfur or liquid $SO_2$ and regeneration of the absorbent. A joint venture, Chemico-Basic, has been formed to market the concept.

Another recent jointly developed process is that of Esso Research and Engineering and Babcock and Wilcox. This process uses absorption on a dry sorbent that can be regenerated, and recovery of the $SO_2$ as sulfuric acid. The process is being tested in a $7 million study, sponsored by a group of power companies, at a plant of Indiana and Michigan Electric Co.; if successful, the companies say, the tests could lead to commercialization by 1973.

### Energy demands

Despite such an array of processes available, it's fair to say that $SO_2$ control is far from a booming business. One possible explanation could be that $SO_2$ emissions have become part of a larger and more complex problem that has come to be called the "energy crisis." Forecasts of sharply rising demands for electric power have proven to be, if anything, too conservative, at a time when other factors are at work which are making it difficult for utility operators to fill the demand for power. Increasingly vocal conservation interests have thwarted plans for base load nuclear power plants and for pumped storage hydroelectric plants for peak power; and coal supplies for fossil-fueled plants are becoming critical. (Coal in itself is not in short supply, but mine operators also miscalculated demand and failed to expand productiton facilities accordingly.)

Thus, faced with the problem of meeting the sharply rising demands for power, utilities seem to be seeking interim solutions for the $SO_2$ problem, and postponing any large capital expenditures—and headaches—that most emissions control processes would entail. For although $SO_2$ emissions have been of concern for some time, and control regulations are becoming more stringent, the fact remains that stack gas cleanup is but one alternative available to meet the standards, and at the moment is not as attractive as switching to low-sulfur fuels.

A case in point is Commonwealth Edison of Chicago, which a few months ago announced its accelerated program for air pollution control which relies heavily on low-sulfur fuels to cut $SO_2$ emissions. The company is almost doubling its purchases of low-sulfur coal, is stepping up the use of natural gas by 50%, and has received a license from the Department of the Interior to import 4.5 million gallons of low-sulfur residual fuel oil. The utility says it is considering an $SO_2$ control process for one of its stations, but announced no firm plans or timetable for the installation.

### Interim solution

But in the long run, the switch to low-sulfur fuels can offer only temporary respite from the $SO_2$ problem. For one thing, low-sulfur coal supplies are limited, which is reflected in the fact that the premium paid for low-sulfur coal has recently risen to $1.50 per ton. Another problem is geographical location of the sources—about 90% of U.S. low-sulfur coal reserves are located in the West, far from the major markets in the East. Commonwealth Edison, for example, will the buy 300 railroad cars to haul its low-sulfur coal in from the far West.

Natural gas' low sulfur content makes it attractive for power generation, but the supply situation for it isn't very bright, either. The American Gas Association recently announced that natural gas reserves declined by 4.2% in 1969, the second successive yearly decline. The figures are for proven reserves only, but in releasing the figures, AGA says that unless the situation is corrected, as by increased exploration, the industry will be severely hampered in trying to supply the clean-burning fuels market.

The situation for low-sulfur fuel oil is somewhat better, but only marginally so. Residual oils from low-sulfur crudes are available from some sources on the world market; desulfurization of high-sulfur residual oil, though more difficult than desulfurization of distillate oils, is at least technically feasible. The major problem with residual desulfurization is cost; the process can add as much as 20 to 30% to the cost of fuel oil. But residual oil desulfurization apparently does have at least a limited market; a company called Fuel Oil Desulfurization, Inc., for example, is planning a $150 million plant at Riverhead, Long Island, to serve the metropolitan New York market with low-sulfur oil.

### If and when

But since coal is still king when it comes to power generation, and with high-sulfur content common with most U.S. reserves, wide-scale adoption of stack gas cleanup to control $SO_2$ is more a question of when, than if. Precisely when will be determined by two factors. The utility industry, perhaps understandably, seems reluctant to adopt any $SO_2$ control process on the basis of the relatively small demonstration units that have thus far been operated. The usual remedy suggested to correct this situation is federal funding of larger demonstration projects.

The other factor relates to the markets available for recovered sulfur—either in the elemental form, as liquid $SO_2$, or as sulfuric acid—since credits for by-product recovery are an important factor in the operating costs of mnay of the processes. The amount of sulfur released as $SO_2$ emissions from power plant boilers could represent a significant share of the U.S. demand but prices for sulfur and sulfur products are notoriously cyclical. And the short-supply, high-price situation which prevailed not too long ago, if anything, has deteriorated.

# ACS sections seek environmental role

## *but recent efforts point up problems*

Now that "environment" is a number one issue in the public mind, those who might be expected to know as much as anyone about the subject—professional scientists and engineers—are engaged in some agonized grappling with problems of organizing meetings so that their expertise can be brought to bear. Although chemists, for example, have traditionally been somewhat aloof from the applications of chemistry in society, changes in recent years have seen them take a far more active interest. The American Chemical Society (ACS) not only launched ES&T in 1967, it also published the much heralded report "Cleaning our Environment: The Chemical Basis for Action," now in its third printing and on its way to becoming something of a best seller.

**Polarization.** *Resolutions of law students produced hostility at* CSW *meeting*

It is at the local level, however, that some of the most interesting developments are taking place. Chemists look around them and see teach-ins everywhere, few if any of them run by chemists. Determination to change this situation has led to the organization of at least two local ACS meetings at which the main focus of attention was "the environment." A day's program at the 5th Middle Atlantic Regional Meeting (MARM), held at the University of Delaware, took as its theme "Chemistry and Environment," while the Chemical Society of Washington (CSW) entitled its one-day symposium at American University (Washington, D.C.), "Will Man Survive His Polluted Environment?"

MARM general chairman Fred T. Wallenberger, a long-time critic of the traditional type of scientific meeting, had definite plans in mind for the MARM. In addition to the usual specialized "by the expert for the expert" sessions (such as those run by the ACS Division of Water, Air, and Waste Chemistry at national ACS meetings), Wallenberger arranged to have papers by experts for nonexperts on the subjects of air pollution, water pollution, space chemistry, and ocean and estuary chemistry. The intention of these sessions was to inform the chemist in areas outside his own narrow specialty, an intention that was satisfactorily achieved to judge from the animated discussion that took place at the Delaware meeting.

While the broadly based sessions during the day were open only to conference attendees (mostly chemists), an 8.00 p.m. public panel discussion at MARM was open to the public. The several hundred people who attended the discussion included representatives of the League of Women Voters, the Sierra Club, and wives of conference attendees. Panel members included Sen. J. Caleb Boggs (R.-Del.); the panel was chaired by ACS board chairman Milton Harris. Wallenberger's intent to have chemists inform the public on environmental matters may not have been realized at the public session, however, since time for discussion was severely curtailed by the late hour at which panel members finished their prepared remarks.

The CSW meeting in Washington was, in contrast to the MARM, in its entirety open to people other than chemists. Several hundred students, including many from Washington area high schools, attended and added considerable spice to the proceedings, cheering speakers on or giving them a hard time in question periods.

An incident which occurred at the CSW meeting neatly polarized the audience and seems to be something of a warning to symposium organizers who, as do the CSW planners, feel that students should be allowed to have their say. Several law students from Georgetown University put five resolutions before the meeting; the law students hoped that CSW would first pass the resolutions at the meeting and then recommend them for adoption by the ACS as a whole. (Sample resolution: ACS members demand that they be able to spend 15% of their salaried time in research, writing, or other productive efforts to solve pollution and other social problems.) The meeting then divided into two factions—one consisting of students, the other of CSW members. Two of the five resolutions were voted down before a CSW member proposed a substitute resolution recommending that CSW and the law students get together to discuss just what it was that the latter were trying to say. This resolution passed and the law students left somewhat miffed.

Although this part of the meeting left a bad taste in the mouths of some CSW members, Dr. Ben Alexander, chairman of the symposium, felt that it was a moderate success. "You can't get action till you get education," he says, "and you can't have both at the same meeting."

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# Trends in pesticide use

## Fate of estuaries linked to the fact that all of us, directly or indirectly, rely heavily on pesticide usage

There are between 850–900 major and minor estuarine systems along the coastline of our country. They are the products not only of the coastal configuration but also of the total land area that drains to them. Thus, bays, inlets, and tidal marshes are modified not only by the fifty million people who live near them but by a large segment of our population living hundreds, if not thousands, of miles away and whose activities markedly influence the amount and quality of the water reaching the estuary.

Since prehistoric times, estuaries have received nutrients from the land through drainage, chemicals in solution, and organic debris. Equally important is the total flow of fresh water from rivers or streams—a vital factor in maintaining reduced salinity. Some estuarine species, such as oysters, live only in brackish water, not in the ocean; juvenile shrimp spend three months in coastal marshes before leaving for the open sea. Many economically important fin fish also use estuarine systems as a nursing ground. Thus, one of the most important problems facing the marine biologist is how to maintain the freshwater supply to estuaries.

Impoundments are springing up along all major river systems to supply water needed for urban centers, industries, and agricultural irrigation. Texas, in developing its statewide water plan, recognized the need to deliver 2.2 million acre-feet of fresh water to Galveston Bay each year if that estuary was to continue to provide 84% of the state's oysters and 69% of the catch of blue crabs, to say nothing of the shrimp and fin fishes.

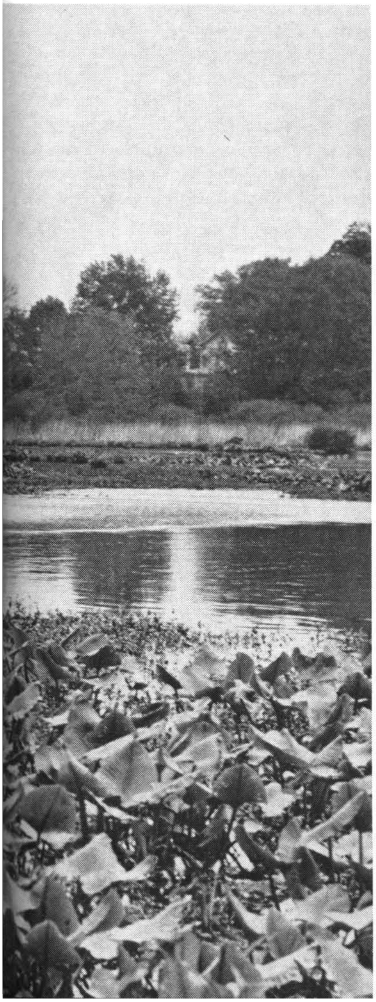
### Vital factors

Human uses of the immediate estuarine system are also vital factors: the cities that crowd the banks; the suburbanite with his bayside, bulkheaded, and channeled retreat; the industries; the shipping; the mining of bays; and most important, the disposal of wastes from all these activities.

The purpose of these statements is to emphasize the complexity of the pollution problem and to suggest that *each estuary is an individual problem.* The nature if the pollutants will depend on agricultural and industrial practices in the region of drainage.

Whether man lives in a nomad's tent, on a farm, in a suburb or in a city, two streams sustain his living quarters. One is air; the other is water. Our influence on these two transport systems is tied directly to the human population density. Both air and water have means to free themselves of waste loads if not overtaxed. Our attention here is necessarily focused on water, yet we need acknowledge the role of air transport. It contributes to the estuarine load—either by fallout of particulate matter or gaseous exchange at the air–water interface.

In moderation, wastes are gratefully received in the estuary, for on them



depends much of the life in our oceans. Tens of thousands of species of living plants and animals feed on these wastes, converting them to energy that can be used by higher life forms. While degradation of organic compounds takes place through ultraviolet and other light rays, through temperature and physical chemical action, degradation by living organisms plays a tremendously important role.

The types of feeders on detritus in any estuary are the products of the types of wastes that have been delivered to that area over a period of years. A new organic compound emerging on the scene must necessarily effect some adaption and realignment of these species. It is entirely possible that the new pollutant is biodegradable, but species essential to degradation of an entirely different pollutant may have already sucumbed. So, in addition to the problem of assuring biodegradability of a given pollutant, we can occasionally anticipate difficulty because of other locally available chemical contaminants.

**Multiple uses**

Many pesticides are no more harmful to the estuary than the multitude of industrial and household chemicals. As a general class they are designed to destroy or repel some living organism, be it bacteria, fungal disease, an insect, a fish, a weed, or a rodent. In this sense they are poisons that must be used carefully but so must medicines or the family car.

A common impression is that pesticides are principally the tools of a farmer and get into streams, lakes, and estuaries from spray drift and runoff from agricultural lands. This is not their principal use. There are some 900 basic pesticide chemicals formulated and marketed in the U.S. under approximately 50,000 brand names. Of the 900, 600 are bactericidal and fungicidal chemicals, half of which are for industrial and household use. The largest selling pesticide registered with the U.S. Dept. of Agriculture (USDA) is chlorine, without which our water supplies, swimming pools, and general sanitation would be in a bad way. The fact is that the householders regularly use as great a variety of pesticide chemicals as any farmer.

A recent compilation shows that federal agencies are spending annually $100 million for research on pests, pesticides, and pest control. The Science Information Exchange, Smithsonian Institution, Washington, D.C., lists over 3700 active research projects involving pesticides. This list does not include in-house research programs of the agricultural industry. Nevertheless, progress in the development of new pesticide chemicals has slowed appreciably, mainly because expenditures as high as $5 million are necessary before the first pound of a new chemical can be sold. It takes five to seven years to develop the necessary information on effectiveness and safety to register a new compound with the USDA.

**Labor savers**

Nevertheless, pesticide chemicals are here to stay, for these reasons:

- They take the place of heavy commitments of manpower. In the U.S., one man with modern machinery and chemicals can farm hundreds of acres of row crops. This has released forty or more persons for other endeavors for every person producing food. Contrast this to the situation in other countries where 70% of the population has to stay on the farm to feed its occupants.
- Today, sanitation is almost solely the task of pesticide chemicals. They are largely responsible for the control of insect-borne diseases such as malaria, endemic typhus, equine encephalitis, and others.
- The production of many goods and services—building materials, air conditioning, and even transportation—receives an unbelieveable assist from pesticides. Any person will use perhaps ten different pesticides each day, often unknowingly, regardless of his profession or geographic location.

In a sparsely settled area, dilution may adequately solve the problem of waste accumulation. But as population increases, the dilution factor ceases to exist, and the seemingly obvious correction is to develop and use only those products that are readily degraded within a matter of days. Laudable as this goal may be, it overlooks many practical considerations. First, we need as much permanent protection as possible in certain fields. We need to impart as long a life as possible to the building materials with which we construct our homes (as with termite control and fungicides that prolong the life of plywood). We need to prolong the life of wooden telephone poles set in the ground, wooden railroad ties, and the timbers of a dock or wharf. Rugs and fabrics are treated against attack by rot and mildew organisms and insects. The struggle to hold the gypsy moth in check was lost when we did not have a pesticide that would give control for one month after application. So, persistence is bad only if the pesticide progressively accumulates under a specific pattern of use, the residue is toxic or otherwise makes unusable a segment of the environment, or it readily moves into and builds up in the food chain.

### Pesticide types

Prior to 1942, many sanitizing and pesticide chemicals were based on metallic elements such as mercury, copper, and arsenic. Organic pesticides were a big step forward in that they are completely degradable, even though a few are too slowly broken down to prevent accumulation under certain application rates. There are, nevertheless, problems in bacterial and fungal disease control for which there is yet no solution other than an organo-metallic pesticide. Fungicides and bactericides will continue to be essential in all operations of our society —industrial, agricultural, and public health. Metals such as mercury, arsenic, lead, zinc, copper, cadmium, thallium, and selenium are useful in this field. But since they are also nondegradable, they will be progressively less used.

At one time, insecticides led in sales of chemical pesticides, but total production has now leveled off. Realignment and new introductions will result from insect resistance or regulation by withdrawal of previously permitted uses. For example, the domestic use of DDT dropped 50% between 1958 and 1967. More recently, removal of specific uses, from federal registration and restrictive legislation by states has significantly reduced amounts of chlorinated hydrocarbon employed.

Almost 75% of the agricultural use of DDT is confined to cotton and tobacco. A significant percentage of the world production of DDT is used in world health programs for the control of malaria river blindness and other insect vector diseases—a task for which DDT has no peer. There have been no introductions of new chlorinated hydrocarbon insecticides for ten years—research and development long ago shifted to shorter-lived organophosphates and carbamates, and these two classes of pesticides will continue to diversify. What is sorely needed for both public health and forest insect control programs is an insecticide having four to six weeks effective life with no tendency to move into the food chain. No such compound is presently in view.

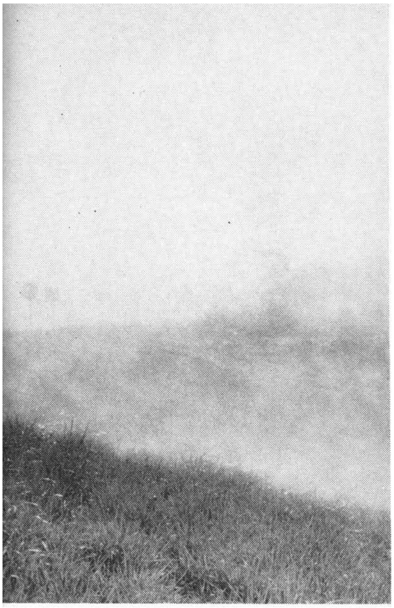
Herbicides have taken over the production lead and play an important role in the manipulation of terrestrial and aquatic plant cover. Thus, the largest number of new compounds will appear in this category. Moderate, not rapid, degradation will characterize most herbicides. Some lands in the southern U.S. may be cropped three times a year, and crop rotation is used to maintain soil structure and fertility. This imposes the requirement that harmful residues should not carry over from one crop to another. Another problem is related to solubility. Some of the water used to irrigate treated fields will be wasted to drainage ditches and may be reused on an entirely different crop. Thus, developers of herbicidal chemicals are well aware that solubility, coupled with persistence, may limit or entirely nullify the usefulness of a candidate product. Many herbicides now in use are tied up in the soils within a few hours after application and thereafter resist leaching.

### Degradation

The greater portion of the pesticides applied to land does not end up in the estuary or ocean. Most chemical pesticides are rather promptly adsorbed by soils, translocated by plants, or dissolved in the waxy surface of vegetation. Photochemical and chemical degradation usually starts immediately after application. A dead insect may convert 50% of the DDT it absorbed to the next lower metabolite. One group of investigators expressed surprise when they exposed oysters in San Francisco Bay and failed to find "expected high levels of pesticides." Please recall that San Francisco Bay is the terminal for the Sacramento and San Joaquin Rivers which drain over 6 million acres of agricultural land that receives heavy annual applications of pesticide chemicals and that oysters under experimental study have shown a capability to concentrate levels of DDT 70,000 times that present in their environment.

On the other hand, the aquatic environment is subject to management through pesticide chemicals, just as the land is. In freshwater impoundments it is frequently necessary to control aquatic vegetation like water milfoil, alligator weed, and water hyacinth. Even more important is the control of filamentous algal blooms. Compounds for this purpose must be reasonably free of adverse effects on subsequent blooms of unicellular algae and zooplankton which are important fish foods. Many new introductions will be made in this field in the immediate future. Residues and side effects on estuarine populations will have to be considered along with residues in edible fish.

Chemicals will also be used in the aquatic environment for the control or management of unwanted fish species. An outstanding example is the use of 3-trifluormethyl-4-nitrophenol (TFM) in the control of sea lamprey in the Great Lakes. The recovery of sport



fishing in Lake Superior and Lake Michigan is due to the use of this pesticide. The Manistee River in Michigan was treated in the fall of 1968 at the cost of $100,000 for the chemical used. Another example would be the use of polychlorinated benzenes for the control of the oyster drill in Long Island Sound. As mariculture develops in this country, there will be an increasing demand for similar chemical tools to manage the estuarine system. In freshwater systems that drain into estuaries, several chemical pesticides, namely rotenone and Antimycin A, are currently used to control trash fish. They are so transient (at least Antimycin A is) that they should not reach the estuary.

## Managing estuaries

The estuarine system, for all its value as a harbor, a recreation area, and a nursery ground for marine life, also has its bad side. It produces hoards of saltmarsh mosquitoes and sand flies. The dog fly breeds in the driftwood at the high tide mark. Cities and resorts in these areas must find relief by treating these areas with pesticides. Shrimp and crabs are little more than aquatic insects and often are endangered by levels of insecticide necessary to control mosquitoes. Fortunately, there are insecticides which can be employed without harm to fish and shellfish. Since development of insect resistance is an ever-present problem, it will be necessary to make repeated introductions of new chemical products for this purpose in the years to come.

There are always new problems. The presence of sea nettles, a species of jellyfish, makes many beaches at times almost unusable for swimming, water skiing, and boating. Sharks plague others. Chemical repellants, as yet undeveloped, offer some promise.

As yet, the contribution of the urban centers to pesticide pollution of the estuarine system has not been mentioned. Preliminary studies indicate that pesticide pollution from this source may be of significant magnitude. The use of pesticides in the home and commercial enterprises to control pests in stored food and fabrics, structural material, home lawns and gardens, parks, and golf courses complicates the picture. It is compounded by the fact that these users are directly tied to storm and sanitary sewer systems. This funnels to the estuary wastes which are insufficiently treated to remove many compounds. It should be noted that sewage systems that do not discharge particulate matter in significant amounts (but there are very few of these) essentially remove all DDT and its metabolites in the process.

Attention must also be directed to a number of chlorinated compounds from urban and industrial sources that mimic and otherwise confuse the amount and effect of chlorinated insecticides found in biological materials. They consist of a number of chlorinated biphenyls, chlorinated naphthalenes, and chlorinated oximes, some of which are exceedingly toxic. It is predicted that chemical pesticides will be at least as varied and numerous in the years ahead. Of course, they will change as pest resistance develops or as compounds having greater effectiveness and safety are found.

## Source control

We cannot depend on the estuarine organisms to degrade an infinite complex of chemical wastes except at very dilute levels. Consequently, chemical wastes will have to be reduced to acceptable levels *at the source*—before they enter the estuary. This will mean approving specific use-patterns in agriculture where drainage waters cannot be concentrated for treatment. In the case of urban and industrial effluents, methods must be found to return the water as free from chemical pollutants as possible.

Adequate monitoring is also invaluable if we are to avoid adverse effects of chemical pesticides on the environment. There is a limit to the safety evaluation that can be required before a chemical has demonstrated its worth. Nor is it practical to attempt to evaluate all of the chemical reactions that *might* take place, given the ever-changing variety of pollutants that could be present in an estuary. Aquatic life in the estuary, if continuously monitored, can alert us to accumulation and unanticipated toxic effects. Chemical analysis for residues in selected living species (including organic debris and plankton) must be broadened beyond the few insecticides on which attention is now focused.

The costs of cleaning up our estuaries and maintaining them at the best possible level for all concerned will be staggering—make no mistake about that. It will not be done overnight. That is impossible. You will find no disagreement in industry or in the Congress or state legislatures on the desirability of the project. But on the subject of how to apportion the available funds needed to run our society, many a compromise will have to be accepted.

**Donald A. Spencer** *is an ecologist with the National Agricultural Chemicals Association in Washington, D.C. He received his A.B. in biological sciences from the University of Denver in 1926, an M.S. in animal ecology from the University of Chicago in 1930, and a Ph.D. in ecology and biological sciences from the University of Chicago in 1958. He has had over 40 years experience as a professional biologist, including 34 years with the U.S. Fish and Wildlife Service. Spencer has also spent five years as chief staff officer, animal biology, with the pesticide division of USDA's research service, and has also been a consulting ecologist on pesticide problems.*

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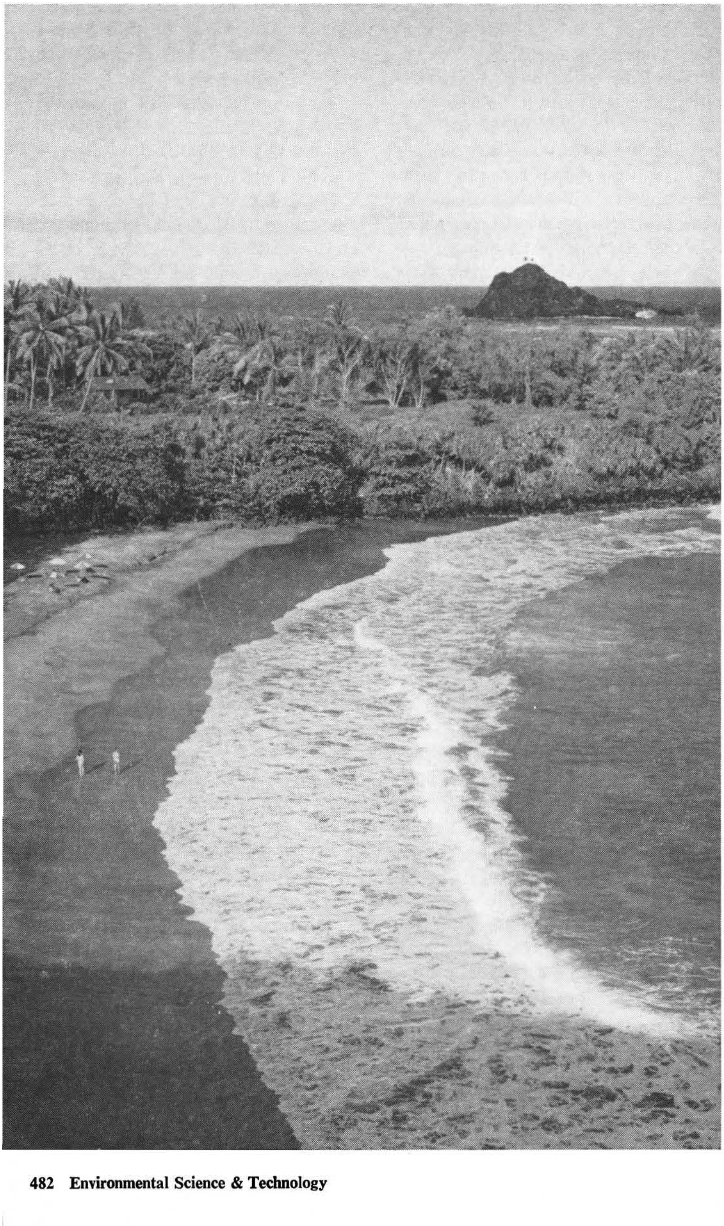
# Gearing up for coastal zone management

## Hawaii's coastal problems are a magnification of those of mainland states



The intense interest of the federal government in the nation's coastal environment is spurring coastal states on to new legislation and activity. Hawaii, California, and Maryland are among those that are devising machinery to deal adequately with coastal problems, which, until recently, were scarcely recognized and, where recognized, were only of local concern.

The change stems from the federal government's pointing out that the coastal assets this nation once had in surfeit are now in jeopardy. The federal government is striving to use what remains of the nation's coastal assets for the benefit of all generations.

Proof of the federal interest was anticipated in the report of the Commission on Marine Science, Engineering, and Resources; given substance in the flurry of bills dealing with the coastal zone introduced into the present Congress; and translated into action when the administration assigned coastal zone responsibilities to the Department of the Interior. The interest is now augmented by the broad look that states are taking at their coastal areas.

Hawaii is the first state to respond to the commission's report by writing a study outlining its consideration of the marine environment. One of the major findings of the study is that the state has much to gain from an understanding of its marine environment and should help pay to acquire such understanding. Working under the auspices of a governor's task force on oceanog-

**Progress.** *Hawaii's goal is to develop its resources without defiling its coast.*

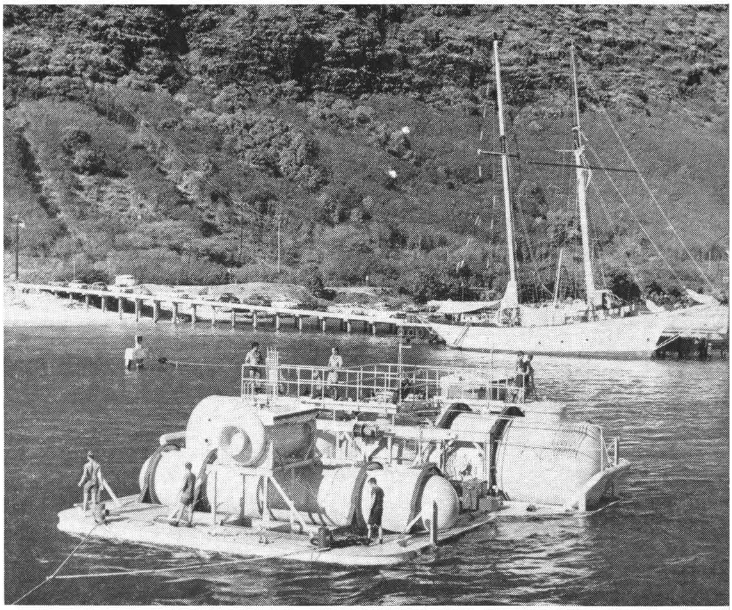
raphy, the citizen's committee that prepared the study recommended an intensive five-year program of research and development in marine matters. This program would be a combined effort by scientists of many disciplines to evaluate the marine assets of the state with the aim of using them to the best advantage of the people of Hawaii and the nation.

Other areas addressed have counterparts in mainland coastal states:

- The need for environmental research, particularly of the physical characteristics of the ocean, which would permit objective analysis of the consequences to our environment of various economic, social, and legal choices. For example, dredging operations to improve a beach or provide a boat channel can change coastal currents and surf conditions, thus altering the balance between processes which add and remove sand in beach areas.
- The need for an oceanographic research park.
- The concept of an International Decade of Ocean Exploration based on the needs of participating nations, from which science programs would be derived. This is somewhat different from the concept that what is good for science is good for the people.
- The need for management of wastes in the coastal zone.
- The possibility of recycling wastes for aquaculture.
- The need for states and universities to have a management structure able to deal uniformly with marine affairs.

Governor John A. Burns of Hawaii has strongly endorsed the study and submitted to the legislature earlier this year a program containing many of its recommendations. Action has already been taken on others, where only executive orders were needed.

Hawaii, as the nation's only island state, has nearly all the marine problems of other coastal states—but in Hawaii they are felt more quickly and personally. The island state can be thought of as a magnifying mirror in which officials of coastal states on the mainland can see a larger image of their own marine problems.



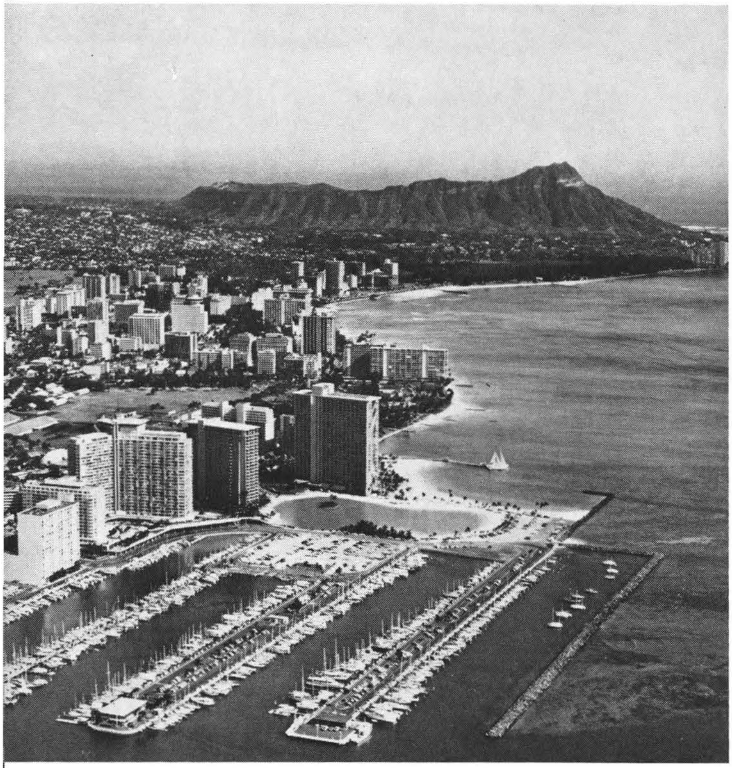
**Research.** *Makai Range undersea habitat being towed to sea from Makapuu*

In the spring of 1969, the students of Hana School of the island of Maui (pop. 41,500) invited Taylor A. Pryor, president of Makapuu Oceanic Center on Oahu, to give a commencement address. They didn't want the usual speech, but instead asked him to answer several questions. How can their island be developed to give them the jobs they see on the mainland but not the pollution and other environmental problems that seem to go along with progress? How can Maui move into the twenty-first century without destroying the beauty of the land or the soul of the people? In other words, they were asking the same question about coastal lands that had been raised a few months earlier by the National Commission on Marine Sciences, Engineering, and Resources—and, more recently, by the federal government and several coastal states in response to "Our Nation and the Sea," the report of the commission. How can we manage coastal areas so that we preserve their environment for recreation, science, and marine life, and yet use them to help satisfy the commercial and industrial needs of modern society?

The students of Hana School saw that commerce and industry had brought environmental problems that are not easily solved by science and technology. Political, economic, and social questions were involved as well. How does one weigh the benefit that coastal industry and shoreline developers bring into a community, through the taxes they pay and jobs they offer, against the cost to the community of giving up some of its beach lands?

### Marine community reacts

Hawaii was the first state to respond to the marine commission's study and write a report as broadly based as "Hawaii and the Sea." For many years the pressures had been building up for such a report. There were problems of a growing tourist industry, where the number of visitors had increased six-



**Waikiki.** *Tourism has played a dominant role in Hawaii's shoreline development*

fold since statehood, and whose chief recreational interests were marine; the need to diversity the economic base of the islands from tourism, agriculture, and defense to other areas, such as an ocean-oriented industry; the obligation of Hawaii to play a major role in the marine affairs of the Pacific basin; and the strong requirement that Hawaii learn as soon as possible the full nature of its living and nonliving marine resources in order to better use and protect them.

The governor's task force on oceanography saw the effect the marine commission report would have on the nation. The study not only gave new stress and direction to marine affairs, but also was based on a new outlook. Therefore, the task force sought to learn what Hawaii's reaction should be and how the state could groom its programs to fit in with national direction. The task force, created by Governor Burns in early 1969, is a highly influential citizen's body made up of leading representatives of the marine industry, the University of Hawaii, as well as the state and federal governments.

An advisory group was formed to organize and lead the study. Very quickly this group and the governor's task force realized that the state first needed a broad action plan for marine affairs, not simply a reaction to the national plan. Once a marine plan for Hawaii was made, its points of coincidence with the national plan could be marked off. These points were numerous, and the advisory group benefitted by having "Our Nation and the Sea" close at hand.

The governor's task force asked that the action plan be drawn up in three months—at first, a seemingly impossible job. There would be no time to do many of the background studies that at first seemed so essential. How is the state organized to handle its marine problems? What is the role of the University of Hawaii in the state's marine affairs? What living and nonliving marine resources does the state have that could be turned to its advantage? And so on.

We found that there was no need to make these studies. In most instances, they would have been a waste of time and money. The state already had many studies of its marine assets, just as other coastal states have, as well as the federal government. Where fundamental studies were missing and critically needed, this fact in itself was a recommendation. The time had come to stop studying and do something. Now was the time to point up the problems and come up with the solutions.

## A plan of action

The writers of "Hawaii and the Sea" shared the marine commission's belief that it is often the administrative and jurisdictional problems rather than the technical ones that impede progress. For example, it does no good to have a way to remove oil after an oil spill if no agency is designated and organized to do the job.

Hawaii needed a plan that was good for the state and acceptable by the people that would be asked to use it. To make it complete, it had to cover all areas of major marine interest. To make it acceptable, those who would put the plan into effect, had to be responsible for drawing it up. These included legislators, scientists, engineers, industrialists, military men, bankers, fishermen, state and federal officials, developers, and journalists.

One hundred carefully chosen volunteers wrote "Hawaii and the Sea," and put to work more than 1000 man-years of pertinent experience. These experts were divided into six task groups:

- Research and development,
- Hawaii's role in the Pacific basin,
- Recreation,
- Environmental quality,
- Living and nonliving resources,
- Role of state and local governments.

Each task group, headed by a chairman and an executive director, held weekly or biweekly meetings and public hearings; made surveys and analyses; drew upon the facilities of the university, the military, industry, and federal, state, and local governments. Their work was coordinated by the advisory group—the parent body—whose members included the chairman and executive director of each task group.

"Hawaii and the Sea" was completed on schedule in 90 days. All of its 76 recommendations are specific and in most instances indicate who should initiate action—the governor, the state, a particular governmental body, or industry. The writers of the report attacked only major issues. The report gives program costs and priorities, so that citizens will know how much they would be paying for a program, and how important it is to pay for it.

From the first day of discussion in the task groups, one theme kept coming up: the need for the state to take a coordinated approach in solving its marine problems. Of what use is it for one state department to approve the development of an oceanographic facility if another department will not release the land put aside for the facility? Similarly, there is no purpose in the state's providing beaches if, in addition, access routes are not assured.

### Role of government

The importance to the nation and to the states of properly managing their marine assets, particularly in their coastal zone where they are most valuable and most vulnerable to abuse, is only now being realized. The problem in the coastal zone began when people wanted to use the same piece of coastline for conflicting purposes—for swimming areas and sewage outfalls, for example—and realized they could not. The National Council on Marine Resources and Engineering Development (Marine Sciences Council) made a thorough study of the problem of multiple use of the coastal zone in 1968-69. Influenced by this work, and by its own findings, the marine commission recommended in its report that each coastal state set up a Coastal Zone Authority "to coordinate plans and uses of coastal waters and adjacent lands and to regulate and develop these areas." As a result of this recommendation, the present national administration put "encouragement of state action for coastal zone planning" at the top of its list of priorities in marine affairs.

It was with this background that the task groups began writing their marine plan for Hawaii. Shortly after the report was finished, the administration made the U.S. Department of the Interior responsible for defining the federal role in coastal zone management. The public works committees in both the House and the Senate are considering bills to develop this role.

The coastal zone is where land and water meet, and the effects of this meeting are pronounced; this is an intuitive definition. The physical extent of the coastal zone is not easily described unless arbitrarily. Legislators and others have tended to leave the definition vague so governments could describe their coastal zone in their own ways, depending on how far they wished to unravel the skein of coastal problems.

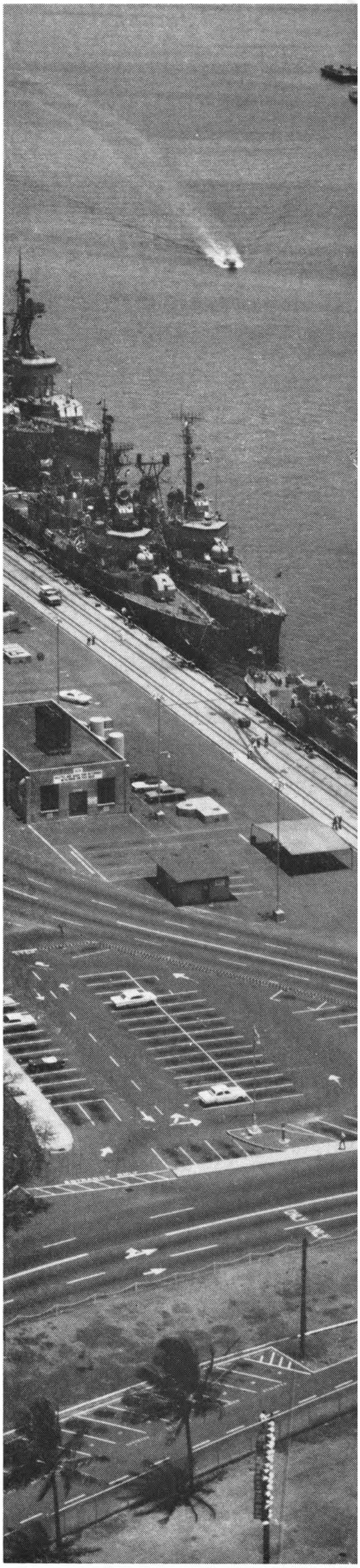
In Hawaii, eight departments in the state government plus the University of Hawaii play parts in marine affairs. For many coastal states, this would be a compact set; for the federal government, it would probably be an answer, not a problem. Still, such a situation does not help Hawaii take advantage of her own intimacy with the sea.

The marine problems of Hawaii are usually major ones that need expeditious solution, and often cut across the responsibilities of several of the state's departments. For instance, a problem of water pollution could involve the Department of Health, which is responsible for enforcing water quality standards; the Department of Land and Natural Resources, which has responsibilities for water resources; the Department of Agriculture, which is involved in problems of erosion, herbicides, and pesticides; the Department of Transportation, whose harbors division is involved in marine facilities; and the department of Planning and Economic Development, which formulates master plans for the development of the state's resources.

Thus, one of the major marine questions in Hawaii was: In the light of the needs of the state and the national stress on effective coastal zone management, how should Hawaii organize its marine activities?

The advisory group did not suggest a separate department to manage marine affairs, even though the marine commission had set a precedent for this recommendation. Departments within the state government already had enough assigned authorities to take care of nearly all of the opportunities and problems that would arise in marine affairs in the foreseeable future. In addition, it did not seem wise to take responsibilties away from departments, even if it were politically possible, when these departments were willing and eager to cooperate on any marine program that could benefit the state and the nation. However, there was no mechanism in the state, short of the governor, able to effect a unified coordinated approach in solving marine affairs problems.

For the preceding two reasons, the advisory group found there was need



**Pearl Harbor.** *Hawaii's harbors and strategic location have played a key role in national defenses* for an executive director for marine affairs in the state government, and describes his duties. He would have a small staff and be responsible for:

- Proposing programs needed to advance Hawaii as a marine state.
- Coordinating activities in marine affairs that cut across the responsibilities of state departments, such as the problems that a coastal zone authority would have to consider.
- Contributing to the work of departments interested in marine affairs.
- Preparing and publishing an annual marine report for the governor detailing both progress and problems.

The advisory group gave much thought about where in the state government the executive director could do his job best. This issue gave rise to the only minority statement in the report. However, most of the advisory group felt that marine questions were so important in Hawaii and involved so many of the departments, that the executive director could work effectively only in the Office of the Governor. This recommendation subsequently won support from Governor Burns. He asked the state legislature to establish such a position directly within his office.

An executive director, or marine coordinator, as the governor designated him, can persuade, argue, cajole, reason, and plead, but only rarely can he command appointees of a governor. Nor would it be legal or even desirable for an executive director to have this power. With this fact in mind, the advisory group recommended that the governor create a Cabinet for Marine Affairs, designating as members the heads of those departments having responsibilities in the marine field. Chaired by the governor, this cabinet would obviously have the power to make and carry out decisions, directly and quickly.

The cabinet would have committees, one of which might be called the Committee for the Beneficial Uses of the Coastal Zone. This would be a working committee, appointed by the cabinet and responsible to it. The committees would develop positions papers and recommendations for the cabinet.

Two points can be made: A Committee for the Beneficial Uses of the Coastal Zone, working in conjunction with the cabinet, could evolve into a state agency able to plan and effect rational use of the coastal zone, as described in the marine commission report, and in proposed federal legislation. Next, the marine cabinet has precedent in the Marine Sciences Council, except that the Hawaiian body would report to a chief executive.

## Coastal zone research

States that wait overly long for federal funds to pay for coastal zone research and planning are similar to the king who, while sitting in front of his fireplace, allowed himself to be roasted to death because his servants had failed to move him. The governor of Hawaii has urged his state legislature to act quickly. "Nationally, there has been delay and uncertainty . . . over the direction and extent of the nation's commitment in marine affairs," he said in his 1970 message. "Hawaii, however, need not wait, but rather should press forward, always conscious of the dangers of cutbacks in federal programs, but nevertheless optimistic that our own programs need not stop while we wait for the federal projects to develop."

With their individual missions in mind, the task groups wanted a dozen or so studies made of the marine resources and environment of Hawaii. They agreed that these studies should stress usefulness to the state, and therefore the shoreline and the nearshore environment and ecology. One of the task groups suggested binding all these studies into one package, which would let researchers work together and share data and facilities. This idea might also appeal to legislators and the public because it is much easier to understand and see the goals of a single effort, even though it has many parts, than to look at the parts individually and wonder if they could be put together, and what they would look like.

With this recommendation at hand, the governor asked the state legislature to appropriate money for an undersea resources survey off Oahu and a Hawaii Marine Resources Atlas. "Hawaii needs much more information about the nature and extent of the resources in the sea surrounding the state," he said. "Sand, precious coral, fish and shellfish, the capacity of the ocean to absorb wastes without contamination—all these need scientific study." The state cannot rationally encourage or regulate the use of its marine resources without knowledge. Industry and the university would work together, using surface and submersible craft and a mobile manned undersea habitat to gather the data, and the university would help assemble the information.

The people of Hawaii, where they have had control, have not abused their coastal zone. Their great love for the sea and the resources in it stems from the ancient Polynesians who once filled the islands, and whose intuitive sense of balancing use and conservation led to a taboo whose results could scarcely be bettered by research. States with a marine shoreline might benefit from the Hawaiian kapu (taboo) that protected overworked sections of reefs, giving them time to regenerate. The penalty for breaking a kapu was death—perhaps too severe a penalty for today.

The children of Hana school see the peril that progress can bring to their island, and yet they want to live in today's world and are asking what can be done. One hundred citizens of Hawaii put their suggestions into "Hawaii and the Sea," and the state is following through.

**William S. Beller** *is on the staff of the Office of Marine Resources of the U.S. Department of the Interior and is chairman of a task force on the federal role in coastal zone research. He also recently organized and now chairs the committee on coastal zone management of the Marine Technology Society. In 1969, at the request of Hawaii's governor, Mr. Beller organized and led a 100-man citizens' group for the preparation of a broad plan for the state's use of its marine resources. He has a B.S. in mechanical engineering and an M.S. in aeronatical engineering from New York University.*

# Spectrophotometric Determination of Atmospheric Fluorides

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■ The lanthanide-alizarin complexan-fluoride reaction has been investigated and an improved procedure for the spectrophotometric determination of atmospheric fluorides is proposed. Optimum reaction conditions have been established and a sampling procedure is proposed which eliminates the interference of diverse ions and molecules commonly present in the atmosphere. The method was found to have a sensitivity of 0.0019 $\mu$g. fluoride per cm.$^2$ and to be reproducible within ±0.003 $\mu$g. per ml. at the 95% confidence level for known concentrations of fluoride of 0.400 $\mu$g. per ml. The proposed procedure is uniquely suitable for the determination of actual fluoride concentrations in ambient atmospheres at parts-per-billion levels.

A sensitive, reliable, and convenient method for determining atmospheric fluorides in the p.p.b. range is one of the greatest analytical needs for the study of air pollution. The critical importance of fluoride pollution in agricultural areas has led an increasing number of states to impose stringent restrictions on the emission of fluorides and on the permissible levels of fluorides in the ambient atmosphere. A method which seems to fill the current requirements—*i.e.*, is both sensitive and free of interferences from normally occurring atmospheric pollutants—has been developed.

The analytical problems in determining very low levels of fluoride in the atmosphere are indeed challenging. It seems generally overlooked that the sampling step itself leads to inherent errors due to the coexistence in the atmosphere of a number of substances incompatible with fluoride when in solution. Therefore, when fluorides are scrubbed from the atmosphere prior to analysis, a number of species containing iron, aluminum, calcium, magnesium, and lead must also be trapped and put into solution along with the isolated fluorides. The resultant formation of insoluble substances, such as calcium fluoride and lead fluoride, must introduce potential interference and certainly the formation of extremely stable complexes, such as the hexafluoroaluminate and the hexafluoroferrate(III), must mask fluorides so that subsequent analytical determinations give values representing fluoride activities after sampling rather than the significant fluoride concentrations of the atmosphere before sampling. The following analytical procedure takes these and other potential interferences into consideration.

Until the work of Belcher, Leonard, *et al.* (1959a) no reaction which produced a positive color change with fluoride was known. In 1959, these workers observed that fluoride forms a soluble, lilac-blue ternary complex with the red cerium(III) chelate of alizarin complexan (1,2-dihydroxyanthraquinonyl-3-methylamine-*N,N*-diacetic acid) in a sodium acetate-acetic acid buffer at pH of about 4.3. Subsequent studies by Leonard and West (1960) and by Greenhalgh and Riley (1961) revealed that lanthanum, praseodymium, neodymium, and samarium also formed similar ternary complexes. This was the only known reaction in which the fluoride ion itself was responsible for the production of a new colored species.

The structure of the ternary complex was elucidated by Leonard and West (1960) through spectral data and Job plots. These data indicated that a 1:1:1 complex is formed between the alizarin complexan lanthanide, and fluoride with a hexacoordinated configuration.

This method has been applied to the determination of fluorine in organic compounds by Belcher, Leonard, *et al.* (1959b) and Johnson and Leonard (1961), in natural waters by Greenhalgh and Riley (1961), as well as by Yamamura, *et al.* (1962), and in deposit gauge samples by Jeffery and Williams (1961). The sensitivity and reproducibility were better than would have been possible with the indirect methods which would be generally susceptible to interference from chloride, sulfate, and various cations. Even though several cations interfered appreciably, the common anions had no effect on the alizarin complexan-lanthanide-fluoride reaction.

The remarkable sensitivity of this reaction prompted investigation into the application of the Belcher reagent to the spectrophotometric determination of atmospheric fluorides.

## *Experimental*

**Preliminary Investigation.** Studies of the alizarin complexan-lanthanide-fluoride reaction and its applications have established various reaction conditions as being optimum. Each set of recommended experimental conditions was investigated for sensitivity and reproducibility. It was determined that the procedure outlined in a short, unpublished work by West, Lyles, *et al.* (1963) gave the best results when supplemented by Belcher and West's suggestion (1961) that the addition of a miscible organic solvent increases the sensitivity of the reaction. This procedure is outlined below.

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[1] Kem-Tech Laboratories, Inc., 16550 Highland Road, Baton Rouge, La. 70800.

Reagents:

Standard fluoride solution (5 μg. per ml.). Dissolve 0.2211 g. of reagent grade NaF in distilled water and dilute to 1 liter. This solution contains 100 μg. fluoride per ml. Dilute to 1:20 to obtain the working solution.

Buffer Solution. Combine 188 g. of anhydrous NaOAc with 336 ml. of glacial HOAc and dilute to 1 liter with distilled water. When this solution is diluted 1:10 with distilled water, the pH should be 4.3.

Alizarin complexan solution ($1 \times 10^{-3}M$). Dissolve 0.40 g. of alizarin complexan (obtainable from K & K Laboratories, Inc., Jamaica, N.Y.) in a minimum amount of dilute NaOH. Add 100 ml. of buffer and dilute to nearly 1 liter. Adjust to pH 4.3 with dilute NaOH or HCl using a pH meter. Dilute to mark.

Cerium(III) nitrate solution ($3 \times 10^{-3}M$). Dissolve 1.30 g. of $Ce(NO_3)_3 \cdot 6H_2O$ in 100 ml. of buffer. Dilute to nearly 1 liter and adjust the pH to 4.3. Dilute to mark.

Procedure:

Add standard fluoride, 10.0 ml. of alizarin complexan, 10.0 ml. of Ce(III), 25.0 ml. of acetone, and dilute to 100 ml. Let stand for 90 min. and determine the absorbance at 618 mμ using 1-cm. cuvettes.

These preliminary experiments indicated that the optimum alizarin complexan concentration in the test solution was $10^{-4}M$.

The substitution of an equimolar lanthanum(III) nitrate solution for the cerium(III) nitrate increased the optical density of a standard solution containing 0.5 μg. fluoride per ml. by nearly 11% (Table I). This confirmed the observations of previous investigators (Belcher and West, 1961; Greenhalgh and Riley, 1961) that the use of a lanthanum-based reagent yields more sensitive results than does the use of other lanthanides.

The addition of acetone to the extent of 25% (v./v.) increased the pH of the test solution from 4.3 to 4.8. Additional sensitivity was noted when the pH was adjusted back to 4.3 with dilute hydrochloric acid (Table II).

The absorption spectrum of the ternary fluoride complex *vs.* a reagent blank (Figure 1), shows that the wavelength of maximum absorption is 618 mμ.

**Development of the Method.** The optimum concentration of the lanthanum(III) and alizarin complexan in the test solution was established in the preliminary experiments as being of the order of $10^{-4}$ *M*. The dependence of optical density on the mole ratio of the reagents (La/A.C., lanthanum/alizarin complexan), and pH was determined concurrently in the following manner. Sufficient standard fluoride solution was added to each of the four 100-ml. volumetric flasks to provide a fluoride concentration of 0.5 μg. per ml. on dilutions. With the amount of $1 \times 10^{-3}M$ alizarin complexan held constant at 10.0 ml., varied amounts of $3 \times 10^{-3}M$ lanthanum(III) were added to give mole ratios, (La/A.C.), of 1:1, 2:1, 3:1, and 4:1. Ten ml. of buffer and 25.0 ml. of acetone were then added in that order, and the solutions were diluted to 100 ml. with distilled water. A set of four test solutions and corresponding blanks was prepared for each 0.1 pH unit from 3.9 to 4.7, the pH being adjusted with dilute hydrochloric acid. An inspection of the data in Table II shows that the optimum pH and reagent mole ratios are 4.1:4.2 and 2:1, respectively.

**Table I. Comparison of the Sensitivities of Lanthanide-Alizarin Complexans**

| Fluoride concentration (μg./ml.) | Absorbance Ce(III) | Absorbance La(III) |
|---|---|---|
| 0.1 | 0.037 | 0.046 |
| 0.3 | 0.123 | 0.141 |
| 0.5 | 0.203 | 0.255 |
| 0.7 | 0.268 | 0.291 |

**Table II. Effect of pH on Sensitivity**

| Fluoride concentration (μg./ml.) | Absorbance pH 4.8 | Absorbance pH 4.3 |
|---|---|---|
| 0.1 | 0.046 | 0.054 |
| 0.3 | 0.141 | 0.166 |
| 0.5 | 0.225 | 0.259 |
| 0.7 | 0.291 | 0.323 |

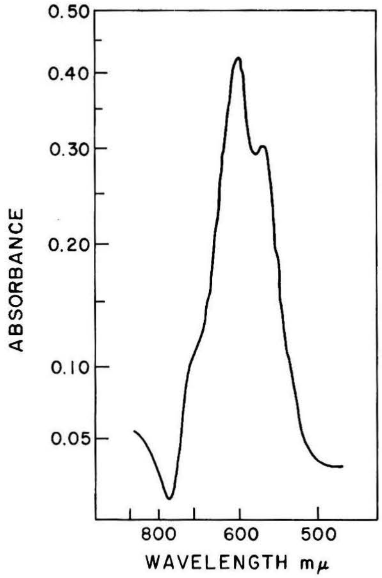

**Figure 1. Absorption spectrum of the ternary fluoride complex *vs.* reagent blank**

Comparison studies of acetone, acetonitrile, methanol, and ethanol as the miscible organic solvent were conducted to determine their relative sensitivity enhancement capabilities.

The procedure outlined under the preliminary investigation was used in this experiment. A series of standard solutions was prepared for each organic solvent, the final concentration of which was 25% (v./v.). Acetonitrile was found to be slightly more effective than acetone in the enhancement of sensitivity, and both were vastly superior to methanol or ethanol (Table IV). Also, acetonitrile has the advantage of being less volatile than acetone. However, acetone was chosen as the miscible organic solvent to be used in the remainder of this investigation because reagent-grade acetone is much cheaper than is practical-grade acetonitrile.

The optimum acetone concentration was ascertained by comparing the optical densities of a series of standard fluoride solutions (0.5 μg. per ml.) containing varied acetone concentrations. To each of four 100-ml. volumetric flasks containing 50 μg. of fluoride was added 10.0 ml. of buffer, 10 ml. of $1 \times 10^{-3}M$ alizarin complexan, 10 ml. of $2 \times 10^{-3}M$

Table III. Effect of pH and Mole Ratio (La/A.C.), Variations

| pH | Absorbance[a] (La/A.C.) 1:1 | 2:1 | 3:1 | 4:1 |
|---|---|---|---|---|
| 3.9 | 0.181 | 0.258 | 0.253 | 0.251 |
| 4.0 | 0.221 | 0.261 | 0.260 | 0.260 |
| 4.1 | 0.223 | 0.264 | 0.262 | 0.260 |
| 4.2 | 0.225 | 0.263 | 0.257 | 0.247 |
| 4.3 | 0.227 | 0.252 | 0.248 | 0.243 |
| 4.4 | 0.230 | 0.245 | 0.245 | 0.233 |
| 4.5 | 0.240 | 0.242 | 0.238 | 0.220 |
| 4.7 | 0.213 | 0.231 | 0.217 | 0.212 |

[a] Fluoride concentration = 0.5 μg/ml.

Table IV. Sensitivity Enhancement by Miscible Organic Solvents

| Fluoride concentration (μg./ml.) | Absorbance No organic solvent | Methanol | Ethanol | Acetone | Acetonitrile |
|---|---|---|---|---|---|
| 0.1 | 0.005 | 0.038 | 0.042 | 0.054 | 0.057 |
| 0.2 | 0.015 | 0.078 | 0.086 | 0.110 | 0.112 |
| 0.4 | 0.055 | 0.156 | 0.162 | 0.214 | 0.220 |
| 0.6 | 0.095 | 0.216 | 0.227 | 0.295 | 0.303 |

lanthanum(III), and 25.0 ml. of acetone. The pH was adjusted to 4.1 to 4.2 with dilute hydrochloric acid. The solutions were diluted to 100 ml. and their optical densities determined at 618 mμ. The sensitivity of the reagent was found to increase as the concentration of the acetone was increased. Though higher concentrations gave better sensitivity, 25% (v./v.) was selected as the optimum concentration because the increased volatility of solutions containing higher acetone concentrations would present problems to the analyst, especially in field operations.

After optimum reaction conditions were established, the buffer was modified by the addition of standard hydrochloric acid so that the desired pH of the test solution, 4.1 to 4.2, would be produced automatically upon the addition of reagents. The lanthanum(III) and buffer solutions were combined to eliminate the separate addition of these reagents.

For the remainder of this investigation the following reagent formulations and procedures were used.

Reagents:

Alizarin complexan ($1 \times 10^{-3}M$). Dissolve 0.385 g. in a minimum amount of dilute NaOH. Dilute to 1 liter with a buffer solution containing 34 ml. of glacial HOAc and 18.8 g. anhydrous NaOAc per liter.

Lanthanum nitrate-buffer ($2 \times 10^{-3}M$). Dissolve 0.866 g. $La(NO_3)_3 \cdot 6H_2O$. Add 222 ml. of glacial HOAc and 890 milliequivalents HCl. Dilute to 1 liter. The pH of this solution, when diluted to 1:10 and containing acetone to the extent of 25% (v./v.), should be 4.1 to 4.2.

Procedure:

To 100-ml. volumetric flasks, add standard fluoride, 10.0 ml. alizarin complexan, 10.0 ml. lanthanum(III)-buffer, 25.0 ml. of acetone. Dilute to mark and determine the optical density at 618 mμ with a Beckman DU spectrophotometer using 1-cm. cuvettes. The results of the study of diverse ion interferences with this method are summarized in Table V. Cations that form stable complexes with fluoride would be expected to interfere by competing with the ternary complex for the fluoride ion. Of the common cations, aluminum interfered to the greatest extent. When this ion was present in equimolar concentrations with the fluoride ion, an interference as great as 50% was encountered. Iron, copper, and zinc interfered to a lesser degree. Lead and cadmium presented even a smaller problem while sodium did not interfere at all when present at 100 μg. per ml.

Table V. Interference of Diverse Ions with the Determination of Fluoride

| Interferer | Added as | Concentration (μg./ml.) | Percentage interference[a] |
|---|---|---|---|
| Aluminum | $AlCl_3$ | 0.01 | −2 |
| | | 0.05 | −5 |
| | | 0.1 | −11 |
| | | 0.5 | −64 |
| Ammonium | $NH_4Cl$ | 100.0 | 0 |
| Cadmium | $CdSO_4$ | 1.0 | 0 |
| | | 10.0 | −1 |
| | | 100.0 | −7 |
| Copper | $Cu(OAc)_2$ | 0.1 | −1 |
| | | 0.5 | −5 |
| | | 1.0 | −18 |
| | | 5.0 | −66 |
| Iron | $FeCl_3$ | 0.1 | 0 |
| | | 0.5 | −1 |
| | | 1.0 | −3 |
| | | 2.0 | −33 |
| Lead | $Pb(OAc)_2$ | 0.1 | 0 |
| | | 1.0 | −2 |
| | | 10.0 | −14 |
| Sodium | NaCl | 100.0 | 0 |
| Zinc | $ZnCl_2$ | 0.1 | −1 |
| | | 0.5 | −8 |
| | | 1.0 | −14 |
| | | 5.0 | −85 |
| Chloride | NaCl | 154.0 | 0 |
| Hypochlorite | NaClO | 100.0 | 0 |
| Nitrite | $NaNO_2$ | 1.0 | 0 |
| | | 5.0 | −5 |
| | | 10.0 | −13 |
| | | 20.0 | −32 |
| Phosphate | $NaH_2PO_4$ | 0.5 | 0 |
| | | 1.0 | 0 |
| | | 5.0 | 14 |
| | | 10.0 | 44 |
| Sulfate | $Na_2SO_4$ | 100.0 | 0 |
| Sulfide | $Na_2S$ | 1.0 | +1 |
| | | 10.0 | +2 |
| | | 100.0 | +5 |
| Sulfite | $Na_2SO_3$ | 10.0 | 0 |
| | | 100.0 | −3 |
| Formaldehyde | | 10.0 | 0 |

[a] Fluoride concentration = 0.4 μg. per ml.

Ammonia, chloride, hypochlorite, sulfate, sulfide, and sulfite were without appreciable effect on standard 0.4 μg. per ml. fluoride solutions, even when present in concentrations as high as 100 μg. per ml. Nitrite, representing atmospheric nitrogen dioxide, did not interfere appreciably unless present in concentrations greater than 4 μg. per ml. An interference of about 5% was noted when 5 μg. per ml. of nitrite was present in a standard fluoride solution of 0.4 μg. per ml. Phosphates,

Table VI. Reproducibility

| Absorbance[a] | µg. F/ml.[b] (calculated) | Absorbance[c] | µg. F/ml[d] (calculated) |
|---|---|---|---|
| 0.112 | 0.202 | 0.214 | 0.398 |
| 0.111 | 0.200 | 0.213 | 0.396 |
| 0.110 | 0.198 | 0.216 | 0.402 |
| 0.112 | 0.202 | 0.213 | 0.396 |
| 0.110 | 0.198 | 0.216 | 0.402 |
| 0.112 | 0.202 | 0.216 | 0.402 |
| 0.114 | 0.203 | 0.215 | 0.400 |
| 0.112 | 0.202 | 0.216 | 0.402 |
| 0.110 | 0.198 | 0.216 | 0.402 |
| 0.111 | 0.200 | 0.216 | 0.402 |
| 0.110 | 0.198 | 0.213 | 0.396 |
| 0.108 | 0.195 | 0.213 | 0.396 |
| 0.110 | 0.198 | 0.215 | 0.400 |
| 0.111 | 0.200 | 0.215 | 0.400 |

[a] Fluoride concentration = 0.200 µg. per ml.
[b] Standard deviation = ±0.002.
[c] Fluoride concentration = 0.400 µg. per ml.
[d] Standard deviation = ±0.003.

which accompany fluorides in the pollution of the atmosphere in the vicinity of phosphoric acid and phosphate fertilizer plants, did not interfere significantly unless present in concentrations greater than 3 µg. per ml.

The reproducibility of the method was studied by determining the optical densities of a series of identical standard fluoride solutions. Fourteen solutions, having concentrations of 0.200 to 0.400 µg. of fluoride per ml., were analyzed. The fluoride concentration of each of the solutions was calculated using Beer's law. The results appear in Table VI.

**Sampling Technique.** Atmospheric fluorides are usually collected for analysis by aspirating the desired air sample through an absorbing solution of distilled water or dilute alkali in a fritted glass scrubber.

The efficiency of the Mine Safety Appliance Co. scrubbers (fritted glass, 30 ml.), with distilled water as the absorbing medium for gaseous fluorides, was determined for various sampling rates. Two of the 30-ml. scrubbers were connected in series with a rotameter by means of Tygon tubing. A source of gaseous hydrogen fluoride was connected to one end of the system and a vacuum source to the other. The hydrogen fluoride source consisted of a dilute aqueous solution of hydrofluoric acid in a polyethylene bubbler. Acid solutions of various concentrations were placed in the bubbler to produce various concentrations of gaseous hydrogen fluoride in the air being passed through the absorbing medium in the two scrubbers. The second scrubber enabled one to evaluate the efficiency of the scrubbing system by determining the amount of hydrogen fluoride that was not absorbed in the first scrubber.

Ten ml. of distilled water were placed in each of the scrubbers and the air sample scrubbed at the desired rate. Then 5.0 ml. of acetone, 2.0 ml. of alizarin complexan, and 2.0 ml. of lanthanum(III) buffer were added. The solution was diluted to the 20 ml. graduation and the absorbance measured. Reagent blanks were prepared in the same manner. The fluoride concentration of the absorbing medium was read from a calibration curve similar to the one in Figure 2. The concentration of fluoride in the air sample was calculated from a knowledge of the total µg. of fluoride and the volume of air sampled. The maximum rate at which air can be drawn through these scrubbers without absorbing medium carryover is about 8 liters per min. At this high sampling rate, the absorbing efficiency was 100%, even with a gaseous fluoride concentration of 10 p.p.m.

The presence of interfering species in the atmosphere, in many instances, necessitates the isolation of the fluoride by steam distillation or ion exchange before analysis. These procedures are tedious, time consuming, and frequently lead to sample loss.

The majority of the interferences can be eliminated quite readily while the air sample is being collected. This is accomplished by placing a prescrubber containing concentrated sulfuric acid between the sample source and the absorption solution. If the prescrubber is heated to approximately 70° C., the volatile acids will pass over into the absorbing solution, leaving any interfering cations trapped in the sulfuric acid.

The volatility of hydrogen fluoride in the prescrubber containing several p.p.m. of aluminum, iron, zinc, and copper was studied by connecting two 30-ml. scrubbers in series with a rotameter and vacuum source. Hydrogen fluoride from a standard source was swept through the heated prescrubber containing concentrated sulfuric acid and the potential interferers under study. Three separate 20-l. samples were drawn through the apparatus as described and three additional samples were taken with the prescrubber omitted. The results obtained from the six samples indicate that the fluoride complexes of aluminum, iron, zinc, and copper dissociate in the scrubber, liberating hydrogen fluoride which is sufficiently volatile under these conditions to ensure its being swept free from any interfering species.

The interference of nitrogen dioxide was not eliminated by this technique. West and Ordoveza (1962) report the elimination of this interference in the determination of atmospheric sulfur dioxide by adding sulfamic acid to the absorbing solution. This reagent decomposes nitrite quantitatively and rapidly, releasing nitrogen gas.

To substantiate this approach for use in the fluoride determination, 10 standard solutions containing 0.2 µg. of fluoride per ml. were prepared. Sufficient sodium nitrite was added to each of the standards to make the final interferer concentration 10 µg. per ml. Sufficient sulfamic acid was added to five of the standards to make the final concentration 0.05%. From the results obtained it was concluded that the inclusion of

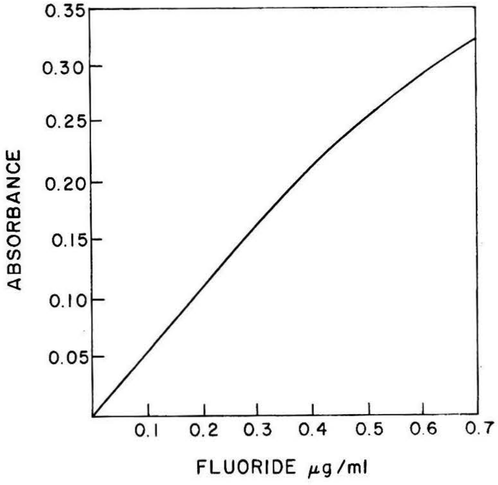

Figure 2. Calibration curve

Table VII. Comparison of Procedures

| | Absorbance | | | | |
|---|---|---|---|---|---|
| μg. F/ml | Ce(III)-A.C.[a] reagent no miscible organic solvent, pH = 4.3 | Ce(III)-A.C. reagent 25% (v./v.) acetone, pH = 4.8 | La(III)-A.C. reagent 25% (v./v.) acetone, pH = 4.8 | La(III)-A.C. reagent 25% (v./v.) acetone pH = 4.1 to 4.2 | La(III)-A.C. reagent 25% (v./v.) acetonitrile pH = 4.1 to 4.2 |
| 0.1 | 0.005 | 0.037 | 0.046 | 0.053 | 0.057 |
| 0.3 | 0.034 | 0.123 | 0.141 | 0.165 | 0.170 |
| 0.5 | 0.074 | 0.203 | 0.225 | 0.259 | 0.265 |
| 0.7 | 0.105 | 0.268 | 0.291 | 0.325 | 0.332 |
| Sensitivity (μg./cm.$^2$) | 0.0073 | 0.0024 | 0.0022 | 0.0019 | 0.0019 |

[a] Alizarin complexan.

sulfamic acid in the absorbing medium completely eliminated the nitrogen dioxide interference.

### *Summary, Discussion, and Recommended Procedure*

The lanthanide-alizarin complexan-fluoride reaction has been systematically investigated as a method for the determination of atmospheric fluorides. The experimental conditions that were found to be optimum are summarized below.

| | |
|---|---|
| Reagent concentrations | Lanthanum(III), 2 × $10^{-4}M$<br>Alizarin complexan, 1 × $10^{-4}M$ |
| Mole ration reagents (La/A.C.) | 2:1 |
| Buffer | pH of 4.1 to 4.2 |
| Miscible organic solvent | Acetone or acetonitrile present at 25% (v./v.) |
| Wavelength of maximum absorption | 618 mμ |

The experimental data obtained concerning the wavelength of maximum absorption and the use of miscible organic solvents agree to a great extent with the results obtained by previously mentioned investigators. Considerable differences were noted, however, in the recommended sampling procedure, reagent concentration, buffer composition, and final test solution pH. The data in Table III clearly indicate that the sensitivity of the method varies considerably with pH and reagent ratios and that maximum sensitivity is realized at a pH of 4.1 to 4.2 and a reagent ratio (La/A.C.) of 2:1.

The comparison data in Table VII are tabulated to illustrate the sensitivity enhancement gained by the use of a lanthanum(III)-based reagent, close adjustment of pH, and the use of a miscible organic solvent such as acetone or acetonitrile.

The order of addition of reagents has an important bearing on the speed of formation of the ternary fluoride complex. If the alizarin complexan is added before the lanthanum(III)-buffer solution, complete color development is attained in less than five min. The color is stable for at least four days.

The stability of an alizarin complexan solution was investigated to determine the aging effect. Test solutions prepared periodically from the same reagent solution proved that the reagent is stable for at least 30 days. The reproducibility was found to be within 0.003 μg. per ml. with 95% confidence at concentration levels of 0.200 and 0.400 μg. fluoride per ml. The standard deviations of these measurements at the above concentrations were ±0.002 and ±0.003 μg. per ml., respectively. The sensitivity of the reagent to fluoride was found to be 0.0019 μg. per cm.$^2$ (Sandell, 1959).

The sampling technique described in the experimental section effectively eliminates the interferences of diverse ions and molecules that are likely to be encountered in atmospheric fluoride surveys.

Excellent sensitivity and reproducibility of the lanthanum-alizarin complexan-fluoride reaction, when coupled with the recommended sampling technique, make this method definitely superior to the indirect methods presently being used in atmospheric fluoride surveys.

### *Acknowledgment*

Special thanks are extended to P. Bourbon, Faculte de Medecine et de Pharmacie, Toulouse, France, for extensive field studies using the method and for his encouraging comments.

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# Gas Chromatographic Identification of Fluoroorganic Acids

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■ Gas chromatographic techniques are described for the separation and identification of fluoroacetate and fluorocitrate from fluoride-injured plant tissue and organs of animals suffering from severe fluorosis. Tissue was extracted with 95% ethanol in a Soxhlet apparatus. The methyl esters of organic acids were separated on columns packed with 10% polyethylene glycol 6000 or 10% Reoplex 400 on Chromosorb W solid phase using a flame ionization detector. Evidence was presented for the occurrence of fluoroacetate and fluorocitrate in forage crops collected near a phosphate plant. The results obtained support the earlier findings suggesting that atmospheric HF may be incorporated into fluoroacetate and fluorocitrate by crested wheatgrass [*Agropyron cristatum* (L.) Gaerth].

Fluoroacetate and fluorocitrate have been shown to occur in soybeans (*Glycine max*, Merr.) treated with atmospheric HF (Cheng, Yu, *et al.*, 1968). More recently, forage crops collected near a phosphate plant were shown to contain these two compounds (Lovelace, Miller, *et al.*, 1968). Although these observations suggest that the biosynthesis of fluoroacetate and fluorocitrate may be a general property of plants, this has not yet been established. These analyses of the fluoroorganic compounds were conducted using paper chromatography, ashing, and fluoride determination. The concentrations reported for these compounds may be too high because of possible contamination with inorganic fluoride.

Horses and cattle grazing near the above-mentioned industrial plant showed severe fluorosis. It was suspected that part of the injury might have been induced by the toxic fluoroorganic acids contained in the hay. A further investigation of the presence of fluoroorganic compounds in the organs of fluorotic animals was thus deemed of interest. Organs of these animals, control animals, crested wheatgrass growing near the phosphate plant, and control plants grown in a greenhouse were obtained and analyzed.

### *Procedures*

Methylfluoroacetate was prepared from monofluoroacetate (Na salt, Sigma Chemical Co.) by dissolving the latter in water, acidifying with 10% $H_2SO_4$, extracting with sulfuric ether, drying the ethereal extract over anhydrous sodium sulfate, and methylating by the method of Colowick and Kaplan (1963).

Trimethylfluorocitrate was prepared from monofluorocitrate (Ba salt, Calbiochem.) by dissolving the latter in 1*N* HCl solution, and removing the barium by addition of $Na_2SO_4$ followed by centrifugation. The solution was then passed through an ion-exchange column (Dowex 50-X, $H^+$ form) and the eluate evaporated to dryness in a rotary evaporator at 40° C. The residue was taken up into methanol and esterified (Colowick and Kaplan, 1963). Treatment with ion-exchange column chromatography facilitated methylation of fluorocitrate and resulted in a higher yield than otherwise.

Samples of crested wheatgrass [*Agropyron cristatum* (L.) Gaerth] were collected within 2 miles of an industrial phosphate plant, air-dried, and ground in a mill. Plants grown in a greenhouse in the absence of significant fluoride were used as controls. Pods of *Acacia georginae*, F. M. Bailey, were treated in a similar manner. Extraction and separation of the two fluoroorganic acids followed the method outlined by Oelrichs and McEwan (1962) who used it originally for studying fluoroacetate in *Acacia georginae.* The final ether extract was condensed and methylated with diazomethane (Colowick and Kaplan, 1963). The methyl esters, after condensation to a small volume (about 0.25–0.5 ml.), were analyzed by gas chromatography.

Kidneys and hearts were obtained from horses and cattle showing severe fluorosis. The organs were blended in a Waring blender containing 95% ethanol for 1 min. followed by extraction for 4 days with 95% ethanol in a Soxhlet apparatus. Other procedures were the same as with plant tissue.

An F & M Model 402 gas chromatograph (Hewlett Packard) was used with a flame ionization detector. Analyses were carried out on dual columns (4-mm. i.d. × 2-m. U-shaped glass columns) packed with 10% polyethylene glycol 6000 or 10% Reoplex 400 (Canvin, 1965) on acid-washed Chromosorb W DMCS (60–80 mesh). Helium was the carrier gas and the column temperature was programmed from 65–215° C. for polyethylene glycol 6000 columns and either from 50- or 60–200° C. for Reoplex 400 columns, all at a rate of 3° C./min.

**Table I. Retention Data of the Methyl Esters of Acetate, Citrate, and Fluorinated Derivatives**

| | Polyethylene glycol 6000[a] | | Reoplex 400[b] | |
|---|---|---|---|---|
| Methyl ester | Retention time (min.) | Temp. (°C.) | Retention time (min.) | Temp. (°C.) |
| Acetate | 0.8 | 67 | 0.7 | 62 |
| Fluoroacetate | 3.6 | 76 | 3 | 68 |
| Citrate | 50 | 202 | 44 | 190 |
| Fluorocitrate | 55 | 213 | 48 | 198 |

[a] Temperature programmed from 65–215° C. at 3°/min.
[b] Temperature programmed from 60–200° C. at 3°/min.

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*Results*

Several columns packed with different liquid phases (including 5% Versamid, 5% diethylene glycol adipate, 10% Tween 80, and 10% polyethylene glycol 20,000) were tested, but only those packed with 10% polyethylene glycol 6000 or with 10% Reoplex 400 on Chromosorb W gave satisfactory results for the organic acid separation. Table I shows the retention data for methylacetate, methylfluoroacetate, trimethylcitrate, and trimethylfluorocitrate separated on these columns. The columns had to be preconditioned and aged for maximum resolution and separation. Columns prepared with less liquid phase would have shortened aging time.

The chromatograms obtained with extracts from plant and animal tissues are shown in Figures 1 through 5. Peaks 1 and 2 were tentatively identified as methylfluoroacetate and trimethylfluorocitrate, respectively, based on retention data and cochromatography.

From the chromatograms of the methyl esters of organic acids extracted from pods of *Acacia georginae* (Figure 1) it is evident that there is a peak (peak 1) in a position corresponding to one produced by an authentic sample of methylfluoroacetate. This was confirmed by cochromatography. The chromatogram lacked a peak which would correspond with one produced by trimethylfluorocitrate.

On the chromatogram of an extract from crested wheatgrass (*Agropyron cristatum*) collected near a phosphate plant there are two peaks of methyl esters (peaks 1 and 2, Figure 2) that corresponded in retention data to those produced by methylfluoroacetate and trimethylfluorocitrate. The positions coincided when authentic esters were cochromatographed (Figure 2). Good resolution of the peaks identified as the methyl esters of fluoroacetate and fluorocitrate was obtained with 10% Reoplex 400 on Chromosorb W (Figure 3). Not all grass samples collected showed the presence of these components. The presence of the components may be related to the specific sampling area in relation to the fluoride source. Further experiments are necessary to establish any correlation between presence of components and sampling area.

**Figure 1. Chromatographic separation of methyl esters of organic acids from pods of *Acacia georginae***

**10% Reoplex 400 on Chromosorb W (60–80 mesh)**

Chromatograms of methyl esters of organic acids from greenhouse-grown crested wheatgrass did not have peaks which corresponded to the two fluoroorganic acids (Figure 4). The dotted lines illustrate cochromatographic positioning of the methyl esters of fluoroacetate and fluorocitrate.

Horses and cows suffering severe fluorosis were sacrificed and organic acid extracts prepared from hearts and kidneys. Chromatograms of the extract from the kidney of a horse gave two peaks which corresponded in retention data with the methyl esters of the fluoroorganic compounds (Figure 5). Cochromatography with authentic samples coincided with the suspected compounds. No positive results were obtained with other samples.

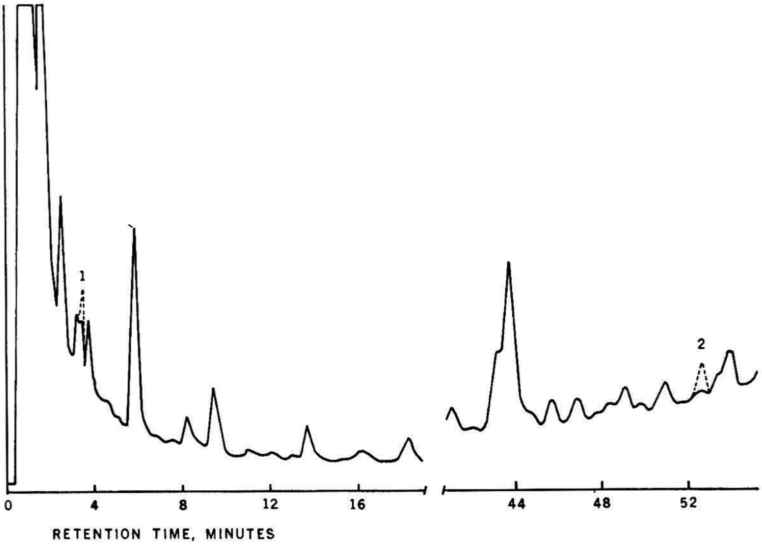


**Figure 2. Chromatographic separation of methyl esters of organic acids from crested wheatgrass (*Agropyron cristatum*) harvested near a phosphate plant**

**10% polyethylene glycol 6000 on Chromosorb W (60–80 mesh)**

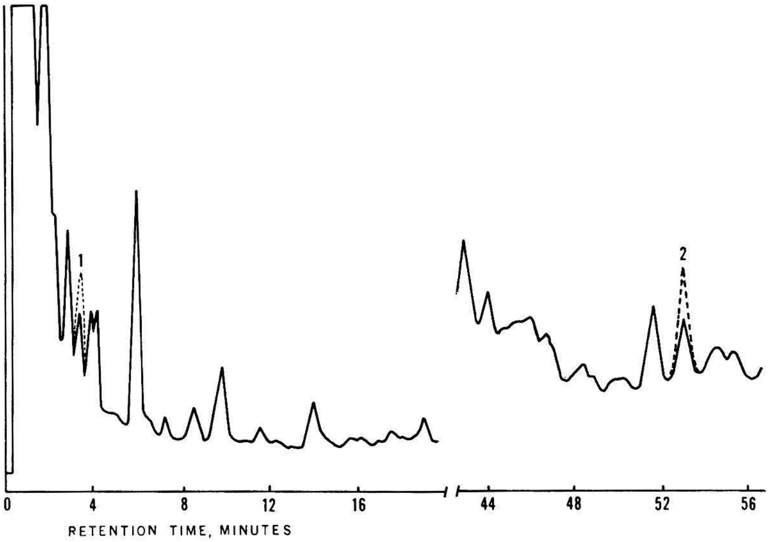


**Figure 3. Chromatographic separation of methyl esters of organic acids from crested wheatgrass (*Agropyron cristatum*) harvested near a phosphate plant**

**10% Reoplex 400 on Chromosorb W (60–80 mesh)**

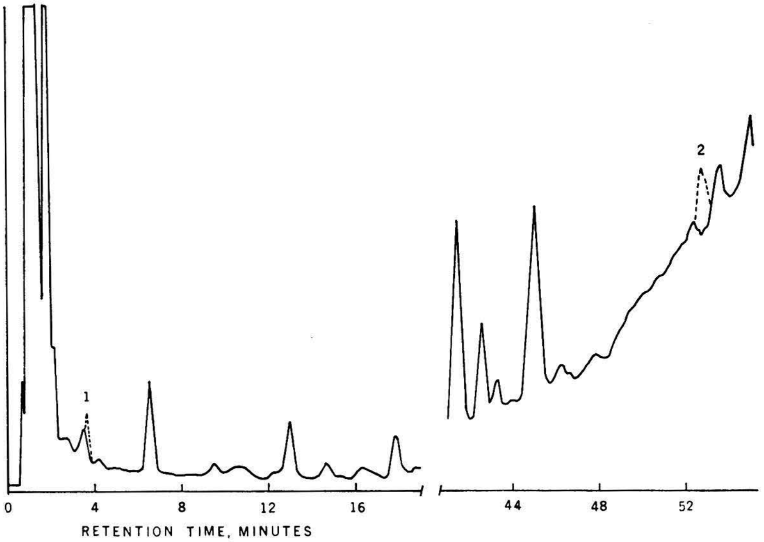


**Figure 4. Chromatographic separation of methyl esters of organic acids from greenhouse-grown *Agropyron cristatum* in the absence of significant fluoride**

**10% polyethylene glycol 6000 on Chromosorb W (60–80 mesh)**

*Discussion*

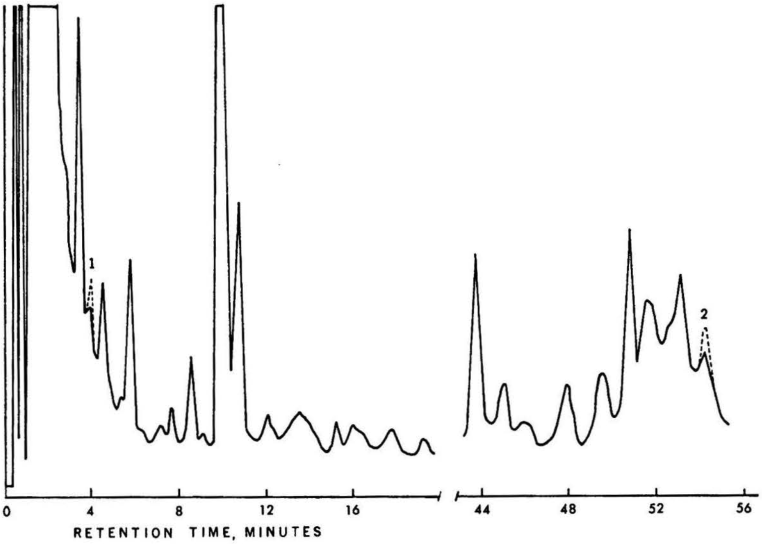
The results obtained indicate the presence of both fluoroacetate and fluorocitrate in some of the fluoride-contaminated tissues that were studied. These together with earlier observations (Cheng, Yu, *et al.*, 1968; Lovelace, Miller, *et al.*, 1968) suggest that atmospheric fluoride may be incorporated by plants into the organic form with the formation of toxic fluoroacetic and fluorocitric acids. Although it has not been established that biosynthesis of fluoroacetate and fluorocitrate may be a general property of plants, some experimental data appear to favor this view. Using fluoro-[$^{14}$C] acetate, Ward and Huskisson (1969) reported the conversion of this compound to fluorocitrate by lettuce. Peters, Shorthouse, *et al.* (1969) reported that extracts of some fluorosed bones from cattle contained fluorocitric acid. The bones of the livestock used in the present study contained high amounts of fluoride (Miller, Yu, *et al.*, 1969). It is possible that part of the fluoride may be present as fluorocitrate. This possibility is now being investigated.

The procedures described in this paper appear to be useful for the separation and the simultaneous identification of both fluoroacetic and fluorocitric acids. The sodium salts of these two acids were added to a control hay sample and carried through the procedures with satisfactory recovery for fluoroacetate but less so for fluorocitrate. In another set of experiments, the ethanol extracts of the hay sample were condensed and passed through ion-exchange columns (Yang and Miller, 1963), and the condensed eluate was extracted with sulfuric ether as described above. No significant difference in the chromatographic patterns was observed between the two procedures.

All the common organic acids are, however, not extracted

**Figure 5. Chromatographic separation of methyl esters of organic acids from kidney of horse that had grazed fluoride-containing hay**

**10% polyethylene glycol 6000 on Chromosorb W (60–80 mesh)**



by the method outlined in this paper. They remain in the aqueous layer after the sulfuric ether extraction, and may be recovered by treatment with column chromatography (Dowex 50-X, $H^+$ form) following neutralization and condensation of the aqueous solution.

With the gas chromatographic techniques described here, nonfluorinated methylacetate and trimethylcitrate could be separated from the fluorocompounds without difficulty, as their retention data were sufficiently different from each other (Table I). It must be mentioned that, although the evidence obtained in the present study indicates the presence of both fluoroacetic and fluorocitric acids in some of the samples analyzed, the results are by no means conclusive and await further investigation.

*Acknowledgment*

The assistance of Esther L. F. Chen, J. L. Shupe, and G. W. Welkie is gratefully acknowledged.

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# Kinetics of Recovering Sulfur from the Spent Seed in a Magnetohydrodynamic (MHD) Power Plant

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■ The open-cycle magnetohydrodynamic (MHD) power plant offers a unique means of profitably recovering sulfur from its effluent gases because of the affinity of the potassium or cesium seeding materials for sulfur and their ease of regeneration. These compounds are added to make the gas electrically conductive and, because of their cost, must be recovered and recycled to the MHD generator. A process which removes the sulfur with hydrogen as hydrogen sulfide from the seed–slag mixture before the seed–slag mixture is recycled to the MHD generator is described and experimentally confirmed. This process allows the power plant effluent gas to be sulfur-free. A kinetic interpretation of the experimental data is presented and these data are used to specify the design and operating conditions for a sulfur recovery reactor for a 1000-MWe MHD power station. The kinetic model applies also to regeneration of the absorbent in the alkalized alumina process now under development for removing sulfur dioxide from power plant stack gases.

The basic nature of the operation of an MHD-topped power plant offers a means not available in a conventional power plant for recovering sulfur from combustion products.

In an MHD-topped power plant, the combustion products are seeded with a potassium or cesium seed to make them electrically conductive. At high temperatures, approximately 2700° K., in the combustor the potassium or cesium seeding materials are completely dissociated into atoms which ionize and thus provide the electrons which give the combustion products their electrical conductivity. Vaporization, decomposition, and ionization of the seed take place at these temperatures regardless of the form of the seed when it is fed to the combustor.

Sulfur removal from the gas phase most likely occurs through reactions of the type shown below:

$$2KO_{(gas)} + SO_{2(gas)} \rightleftharpoons K_2SO_{4(gas)}$$

$$K_2SO_{4(gas)} \rightleftharpoons K_2SO_{4(liq)}$$

Thermodynamic studies (Feldmann, Simons, *et al.*, 1967, a and b) show that removal of the sulfur from coal combustion products is stoichiometric if the system is at equilibrium. This degree of removal is confirmed by unpublished experimental studies in which coal seeded with potassium carbonate was burned. Other experimental studies (Hals and El Bindari, 1964; Hart, Laxton, *et al.*, 1964) establish that potassium sulfate is the main potassium-containing condensation product from sulfur-containing potassium seeded flames.

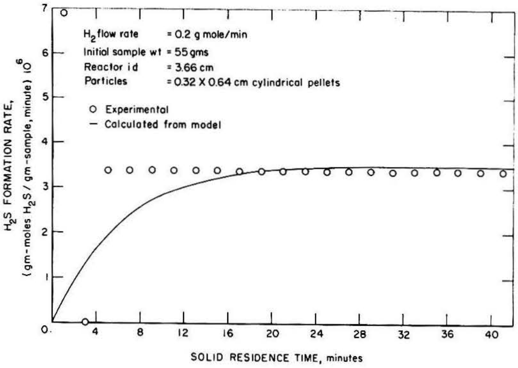

**Figure 1. Differential $H_2S$ formation rate for the reaction of fused $K_2SO_4$–$SiO_2$ with $H_2$**

**temperature = 700° C., $H_2$ partial pressure = 1 atm.**

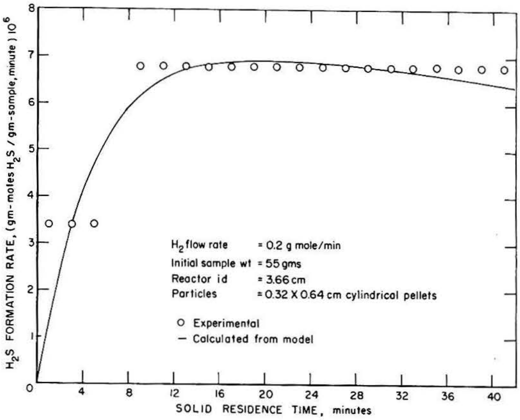

**Figure 2. Differential $H_2S$ formation rate for the reaction of fused $K_2SO_4$–$SiO_2$ with $H_2$**

**temperature = 725° C., $H_2$ partial pressure = 1 atm.**

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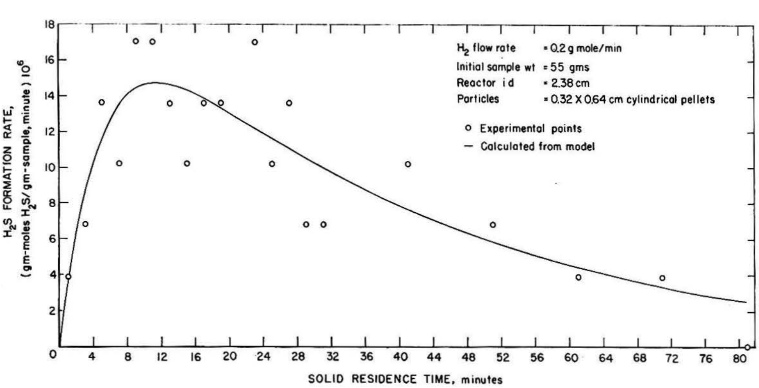

**Figure 3. Differential $H_2S$ formation rate for the reaction of fused $K_2SO_4$–$SiO_2$ with $H_2$**

**temperature = 760° C., $H_2$ partial pressure = 1 atm.**

For the MHD-topped power plant to be economically feasible, recovery of the seed material must be virtually complete. Hence, the MHD-topped power plant must have a means of recovering the seed from the combustion products and recycling this seed to the generator. We propose to take advantage of the chemistry and nature of the MHD-topped power plant operation to eliminate air pollution from sulfur oxides as well as to provide an economically attractive means of recovering the sulfur in coal. To achieve these goals it is necessary to remove the sulfur from the seed–slag mixture before recycling the mixture to the generator. This process should remove the sulfur from the seed–slag mixture in a form that can be readily converted to a salable product.

This paper describes our experimental and kinetic analyses of a process to convert the sulfur in the seed–slag mixture to hydrogen sulfide with a hydrogen feed gas. The hydrogen sulfide can then be separated from the hydrogen by stripping with an ethanolamine solution and converted to elemental sulfur *via* the conventional Claus oxidation process

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

The kinetic model developed is also applied to the regeneration of alkalized alumina with hydrogen.

## *Experimental*

**Preparation of Simulated Seed–Slag Mixture.** To simulate a seed–slag mixture such as would be recovered from an MHD plant a 4.6:1 mole ratio of $SiO_2$–$K_2SO_4$ was mixed by ball milling and then fused at 1150° C. (the approximate dew point of $K_2SO_4$ in combustion products of sulfur-containing fuels) for 48 hours. Some sulfur loss was experienced during the fusion as the sulfur analysis of the fused mixture was about 4 wt. % compared to 7 wt. % for the original $SiO_2$–$K_2SO_4$ mixture. The fused mixture was again ball milled and then formed into 0.32 × 0.64 cm. cylindrical pellets. These pellets constituted the feed for the experiments.

**Operation.** Except where otherwise noted, 55 grams of sample were charged to the reactor, which was for most of the tests a Vycor tube 2.38 cm. i.d. The reactor was heated under nitrogen pressure to the desired temperature and hydrogen was then admitted through a quick opening valve. Hydrogen flow rates were maintained at 0.2 g.-mol/min. for all the tests as this was found to approximate differential operations and, at the same time, to give measurable (0.1 to 2 mole %) hydrogen sulfide concentrations. Except where otherwise noted by data points, gas samples were taken every 2 min. over the first 30 min. and every 10 min. thereafter. The system was designed to minimize backmixing effects by having the "dead" volume between the top of the solid charge and the gas sampling manifold only 33 cm.[3] and gas analyses indicate that these effects were negligible.

The sulfur removal rate was calculated from the data by the formula

$$r = Gy_{H_2S}/W_0$$

where $r$ is the $H_2S$ formation rate in gram-moles ($H_2S$ per gram of sample per minute), $G$ is the gas flow rate in gram-moles per minute, $y_{H_2S}$ is the mole fraction of hydrogen sulfide, and $W_0$ is the initial weight of solid sample. The conversion to hydrogen sulfide as a function of solid residence time was obtained by graphically integrating $r$.

## *Results and Discussion*

The kinetic model is based primarily on the following experimental observations:

The initial reaction rate is zero and increases over a time interval that depends on temperature to a maximum value, *e.g.*, at 875° C. (Figure 7), this time is 1 min. or less, at 800° C. (Figure 6), it is approximately 6 min. Similar behavior is also shown in Figures 1 through 5 for other temperatures.

The maximum conversion level that can be achieved is also a function of temperature. For example, at 875° C. only 4% of the sulfur can be converted before the reaction rate decays to zero; at 760° to 800° C. roughly 50% of the sulfur can be converted to $H_2S$.

One interpretation of the above experimental results is that initially the sulfur is in a state which will not react to form hydrogen sulfide. However, upon exposure to the reaction conditions the original inactive sulfur compound transforms to an active intermediate which reacts to form hydrogen sulfide. Thus, the hydrogen sulfide production rate reflects the concentration of active intermediate which starts at zero, rises to a maximum, and then decays with increasing time.

The decay of the hydrogen sulfide production rate to zero before sulfur conversion is complete can be accounted for by assuming that concurrent with the formation of an active intermediate, which reacts with hydrogen to form hydrogen sulfide, is the formation of a sulfur compound which is refractory to hydrogen. With these assumptions about the chemistry, several equally plausible reaction models can be proposed. However, the rate equations corresponding to these different models are all of the same form making it impossible to distinguish between them on kinetic grounds.

Also, although X-ray analysis has been attempted, chemical

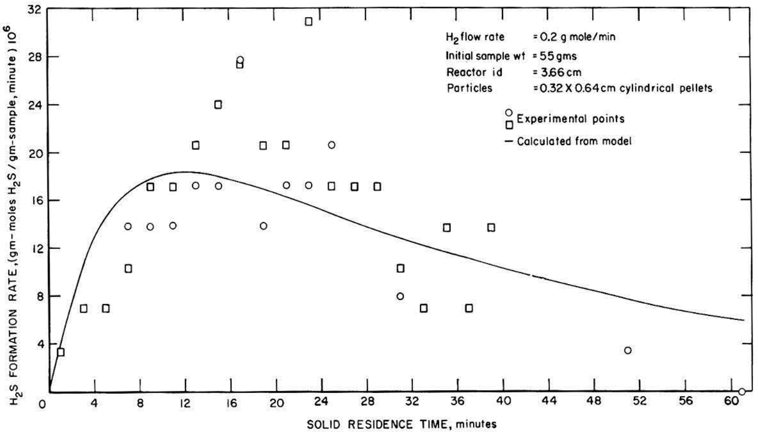

**Figure 4. Differential $H_2S$ formation rate for the reaction of fused $K_2SO_4$–$SiO_2$ with $H_2$**

**temperature = 775° C., $H_2$ partial pressure = 1 atm.**

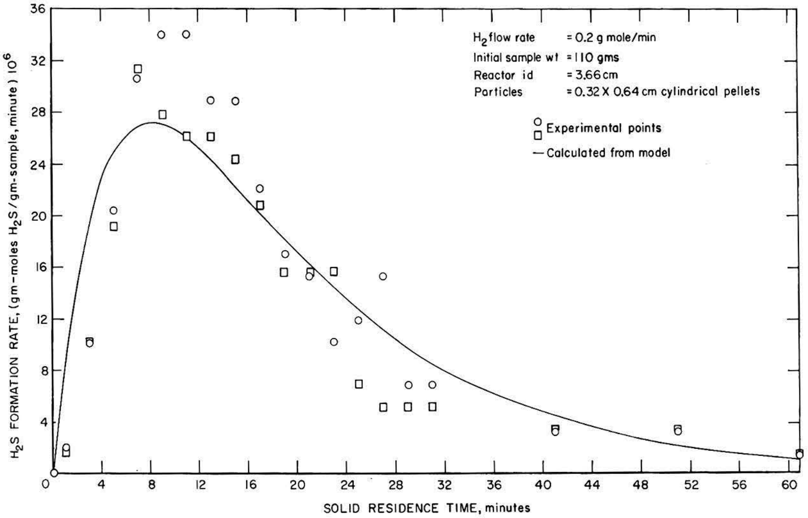

**Figure 5. Differential $H_2S$ formation rate for the reaction of fused $K_2SO_4$–$SiO_2$ with $H_2$**

**temperature = 775° C., $H_2$ partial pressure = 1 atm.**

identification of the actual species present has not yet been achieved. Thus, we chose to use the simplest physically feasible reaction scheme to derive the rate equations with which to analyze the data.

We assume in our model that the sulfur is in an initial state, $I$, which, under reaction conditions, is transformed into an active sulfur containing species $A$ as well as a sulfur species $R$ refractory to hydrogen. The chemical reactions occurring in the system are postulated as

$$I \xrightarrow{k_1} A \quad (1)$$

$$A + H_2 \xrightarrow{k_2} H_2S \quad (2)$$

$$I \xrightarrow{k_3} R \quad (3)$$

where $k_1$, $k_2$, and $k_3$ are reaction rate constants. We take all of the above reactions to be first order with respect to the concentration of solid reactants.

Since the hydrogen partial pressure in this series of experiments is kept constant, $k_1$, $k_2$, and $k_3$ are completely determined by the temperature although, in general, they are also dependent upon hydrogen partial pressure.

The reaction of primary interest is Reaction 2 since it removes sulfur from the solid sample and produces the hydrogen sulfide which can be converted to the desired elemental sulfur. At constant hydrogen partial pressure the rate of hydrogen sulfide production is taken to be

$$r = k_2(A) \quad (4)$$

The concentration of $A$ as a function of time can be found by solving the following differential equation

$$\frac{d(A)}{dt} = k_1(I) - k_2(A) \quad (5)$$

which describes $A$'s net formation where the concentration of $I$ is obtained by solving the differential equation

$$-\frac{d(I)}{dt} = (k_1 + k_3)(I) \quad (6)$$

describing $I$'s disappearance. From Equation 6 we have $(I) = (I_o)e^{-(k_1+k_3)t}$ where $(I_o)$ is the initial concentration of sulfur in the solid. Substituting this value for $(I)$ in Equation 5 gives

$$\frac{d(A)}{dt} = k_1(I_o)e^{-(k_1+k_3)t} - k_2(A)$$

whose solution is

$$(A) = \frac{k_1(I_0)}{k_2 - k_1 - k_3}\left[e^{-(k_1+k_3)t} - e^{-k_2t}\right]$$

Thus, in view of Equation 4, we see that the rate of hydrogen sulfide production is given by

$$r = \frac{k_1k_2(I_0)}{k_2 - k_1 - k_3}\left[e^{-(k_1+k_3)t} - e^{-k_2t}\right] \tag{7}$$

For the regeneration of fused $K_2SO_4$–$SiO_2$ mixtures our data indicate that in the neighborhood of 800° C., $k_1 + k_3$ is approximately equal to $k_2$.

Since

$$\lim_{k_1+k_3\to k_2}\left(\frac{1}{k_2 - k_1 - k_3}\left[e^{-(k_1+k_3)t} - e^{-k_2t}\right]\right) = -\frac{\partial}{\partial k_2}\left(e^{-k_2t}\right) = te^{-k_2t}$$

we use the formula

$$r = k_1k_2(I_0)te^{-k_2t} \tag{8}$$

for the rate of hydrogen sulfide production when $k_1 + k_3 = k_2$.

Equation 7, or 8 if appropriate, is used to correlate the directly measured rate data. Integration of Equation 7 or 8 enables us to compare predicted conversion to hydrogen sulfide with experimentally determined conversion obtained by graphical integration of the measured rate data. Values for the coefficient $[k_1k_2(I_0)]/(k_2 - k_1 - k_2)$ or $k_1k_2(I_0)$ and exponents $(k_1 + k_3)$ and $k_2$ are selected on the basis of the best least-squares fit of Equation 7 or 8 to the rate data.

Calculated values of hydrogen sulfide generation rates using these constants are shown for the fused $K_2SO_4$–$SiO_2$ mixtures in Figs. 1 through 7 for temperatures of 700°, 725°, 760°, 775°, 800°, and 875° C. Examination of these results indicates considerable scatter in the rate data between 725° and 800° C. We attribute this scatter to the large variation in reaction rate with temperature, which is clearly evident in Figs. 1 through 7. Not only does the shape of the reaction rate *vs.* time curve change drastically in the temperature span from 700° to 875° C., but there is also a pronounced variation in the magnitude of the reaction rates. This variability coupled with inability to reduce temperature gradients in the sample much below 10° to 20° C. makes it impossible to exercise better control over reaction rate fluctuations. Running many duplicate determinations of rate *vs.* time as shown in Fig. 6 at 800° C. and using the average value for each time tend to smooth the rate data considerably.

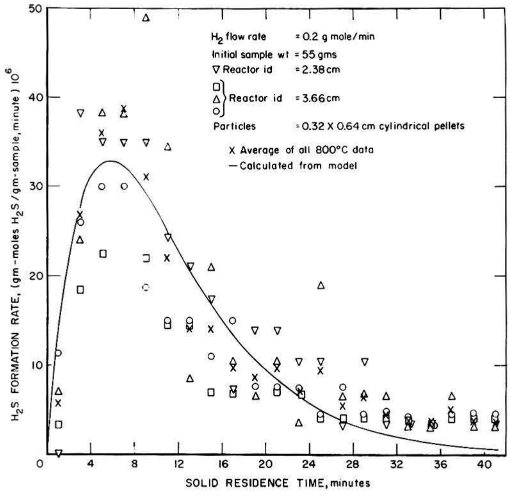

**Figure 6. Differential $H_2S$ formation rate for the reaction of fused $K_2SO_4$–$SiO_2$ with $H_2$**

**temperature = 800° C., $H_2$ partial pressure = 1 atm.**

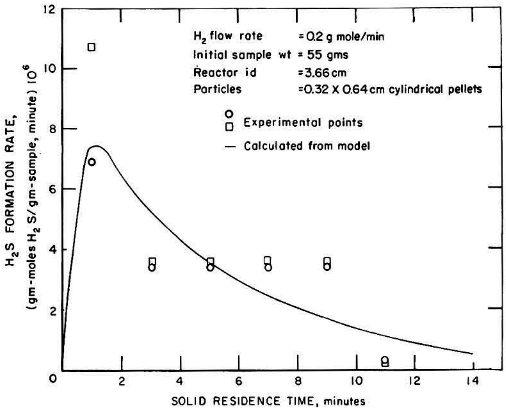

**Figure 7. Differential $H_2S$ formation rate for the reaction of fused $K_2SO_4$–$SiO_2$ with $H_2$**

**temperature = 875° C., $H_2$ partial pressure = 1 atm.**

Experimental levels of sulfur production gotten by integrating the rate data are compared in Figure 8 with those calculated by analytically integrating Equations 7 and 8. The agreement between predicted conversion and measured conversion is well within the experimental error, especially when one considers that the errors in the integral data are cumulative and that relatively few data points past 31 or 41 min. are taken. The scatter that does exist would have been further reduced if the least-squares fit were based on the integral data rather than on the rate data. Thus, the derived rate equations can be used with good accuracy to predict the effect of reactor size on sulfur production over a wide range in shape of $r(t,T)$ curves.

**Effect of Temperature.** In fitting Equations 7 and 8 to the rate data, the groups involving the reaction velocity constants are evaluated rather than the constants $k_1$, $k_2$, and $k_3$ themselves. That is, if $k_2 \neq k_1 + k_3$ then the coefficient $[(I_0)k_1k_2]/(k_2 - k_1 - k_3)$, and the exponents $k_1 + k_3$ and $k_2$ are the terms determined by the least-squares fit, whereas if $k_1 + k_3 = k_2$ then the coefficient $k_1k_2(I_0)$ and the exponent $k_2$ are the quantities calculated.

The effect of temperature on $k_1 + k_3$, $k_2$, and $[(I_0)k_1k_2]/(k_2 - k_1 - k_3)$ is shown in Figures 9 and 10, respectively. The reason for the hyperbolic behavior of the group $[(I_0)k_1k_2]/(k_2 - k_1 - k_3)$ becomes clear when one takes into account that for small values of $k_1 + k_3$ relative to $k_2$ its essential behavior is that of $(I_0)k_1$, but as $k_1 + k_3$ increases, the dominating effect becomes the fact that

$$\lim_{k_1+k_3\to k_2}\left(\frac{(I_0)k_1k_2}{k_2 - k_1 - k_3}\right) = \infty$$

Although Equation 8 is strictly applicable only when $k_1 + k_3 = k_2$, it provides a satisfactory fit even to data well away

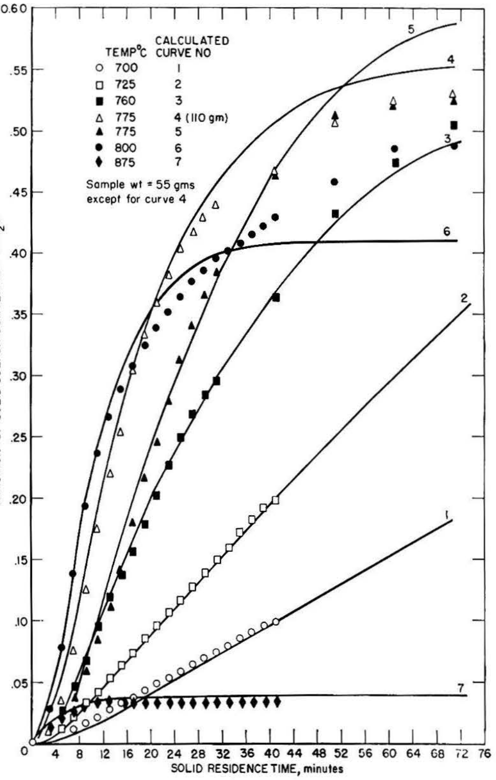

**Figure 8. Effect of temperature and solid residence time on sulfur conversion to $H_2S$**

**$H_2$ partial pressure = 1 atm.**

from this constraint. Thus, the problem of the inherent inaccuracy in the evaluation of large values of $[(I_0)k_1k_2]/(k_2 - k_1 - k_3)$ can be avoided by using Equation 8 when $k_1 + k_3$ is near $k_2$. For $k_1 + k_3 > k_2$, $[(I_0)k_1k_2]/(k_2 - k_1 - k_3)$ is negative and for large values of $k_1 + k_3$ relative to $k_2$ its essential behavior is that of $[-(I_0)k_1k_2]/(k_1 + k_3)$. Thus, for high temperatures (above 800° C. in our study) the values of this group lie on a curve which is similar to the reflection of its graph generated at low temperatures (below 800° C.) in the opposite quadrant.

Knowing the initial concentration of sulfur, $(I_0)$, allows the calculation of separate values for $k_1$ and $k_3$. Figure 9 shows the dependence of these separate values on temperature. With this information the behavior of the system as a function of time and temperature can be explained.

For example, the experimental limitations of sulfur conversion to hydrogen sulfide are explained in terms of the formation of the solid sulfur compound, $R$, which will not react with hydrogen. The rate of formation of $R$ is, according to our model, $d(R)/dt = k_3(I)$ and, as was seen from Equation 6 $(I) = (I_0)e^{-(k_1+k_3)t}$. Thus, the concentration of residual sulfur is

$$(R) = \frac{k_3(I_0)}{k_1 + k_3}[1 - e^{-(k_1+k_3)t}]$$

The maximum conversion level to hydrogen sulfide is achieved when $t = \infty$ and is, at any given temperature, $[(I_0) - (R)(t = \infty)]/(I_0) = 1 - [k_3/(k_1 + k_3)]$. The maximum conversion level of sulfur to hydrogen sulfide, shown in Figure 11, is therefore a function of temperature only. According to the model, this maximum is approximately 80% and should occur around 730° C. Unfortunately, our experiments at 700° and 725° C. were terminated well before the maximum conversion was approached. However, at the other temperatures studied residence times were sufficiently long to enable close approach to maximum conversion. These data are compared with those predicted by the model in Fig. 11.

Both the maximum conversion data in Fig. 11 and the reaction rate data in Figs. 1 through 7 indicate that operating at temperatures either above 800° C. or below 725° C. would not be practical. The optimum temperature depends on the sulfur level of the particular coal used and the effect of reactor size on the process economics.

As Fig. 9 indicates, above 725° C. $k_2$ is independent of temperature. This could mean that above 725° C. $k_2$ represents an

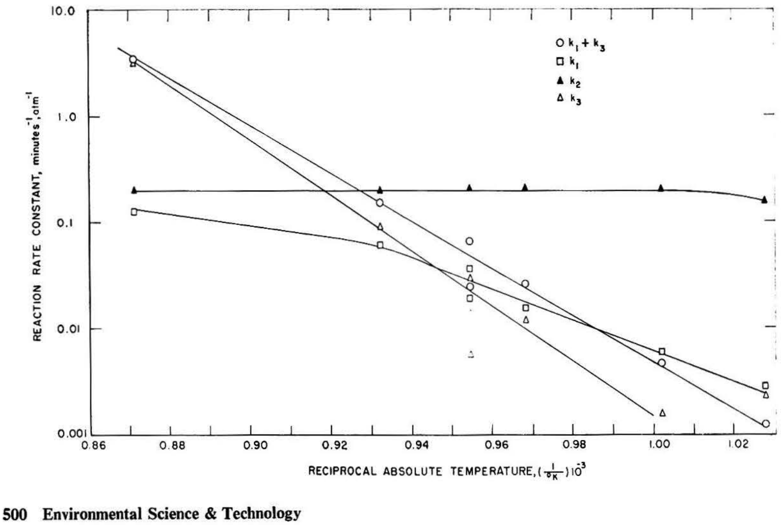

**Figure 9. Effect of temperature on reaction rate constants for the reaction**

**fused $(K_2SO_4\text{-}SiO_2) + H_2 \rightarrow H_2S$**

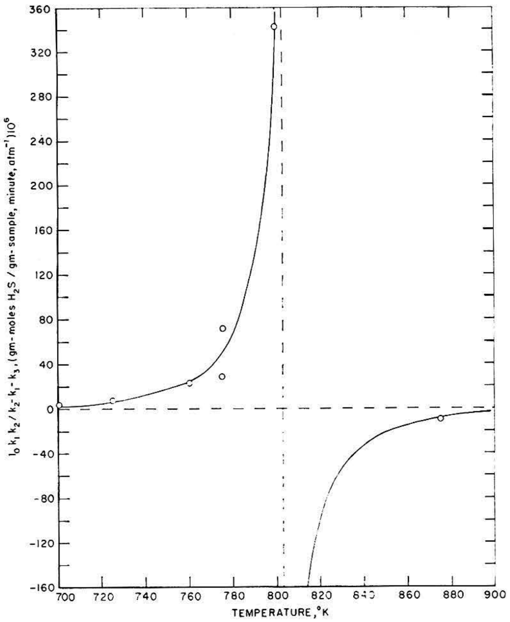

Figure 10. Effect of temperature on the rate coefficient $\frac{k_1 k_2 I_0}{k_2 - k_1 - k_3}$

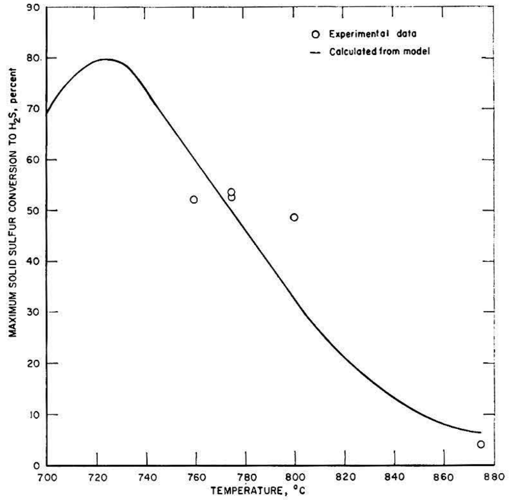

**Figure 11. Variation of maximum sulfur conversion to $H_2S$ with reactor temperature**

**$H_2$ feed, $K_2SO_4$–$SiO_2$ fused mixture**

effective gas film or particle diffusivity rather than a chemical reaction rate constant. Even though no experiments were performed at varying gas velocities or with different particle sizes to establish the effect of diffusion on $H_2S$ formation rates, it is informative to establish the maximum benefit which would result by reducing diffusional resistances by, for example, decreasing particle sizes and/or increasing gas velocities. Under these circumstances $k_2$ would be much greater than $k_1 + k_3$ and the maximum hydrogen sulfide formation rate would be approximately $r_{\max} = k_1(I_0)e^{-(k_1+k_3)t}$. Thus, increases in the specific gas flow rate above that used in our present experiments or operation with finer particles should, at most, allow conversion rates to increase to the values indicated by $r_{\max}$. However, even if the value of $k_2$ can be increased the maximum conversion to hydrogen sulfide will remain fixed because it depends only on $k_1$ and $k_3$.

**Application of Model to Regeneration of Alkalized Alumina.** Hydrogen sulfide formation rates with hydrogen and sulfur-saturated alkalized alumina were measured at 680° C. to see if the same kinetic model could be used to describe this apparently similar reaction system. The comparison, shown in Figure 12 verifies that the model also describes the kinetics of regenerating alkalized alumina. This similarity of regeneration kinetics indicates that techniques for regenerating alkalized alumina (Bienstock, Field, *et al.*, 1967) can also be utilized to remove sulfur from seed–slag mixtures.

**Feasibility of Removing Sulfur from Recycling Seed–Slag Mixtures.** While no detailed estimates have yet been made on

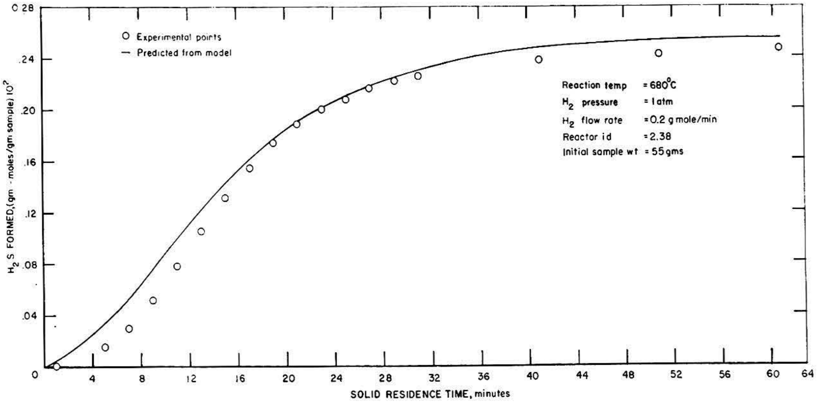

**Figure 12. Comparison of measured $H_2S$ conversion with that predicted by kinetic model for the regeneration of spent alkalized alumina with $H_2$**

the costs of removing sulfur from recycling seed–slag mixtures, it is possible to make an estimate of the major items of equipment that would be needed to remove sulfur from the recycling seed–slag mixture. For example, the sulfur production rate of a 1000 MWe MHD-topped power plant having a thermal efficiency of 0.47 and using a 13,610 Btu/lb. 3 wt. % sulfur coal for fuel will be 383,000 pounds per day which, at a value of $40 per 2240 pounds, is worth $6830 per day. Such a plant will be seeded with about 2 g.-mol. $K_2O$ per kg. of coal. With this seeding level, 47% of the sulfur content in the recycling seed–slag mixture will have to be converted to hydrogen sulfide each pass to ensure a sulfur-free power plant effluent gas. Using a fluid-bed seed–slag regeneration reactor (to avoid complication of varying hydrogen partial pressure in the reactor) operating at a pressure sufficient to maintain a 1 atm. hydrogen partial pressure, we find from the data in Figure 8 the solids residence time needed to achieve the desired conversion level is 40 min. at 775° C. This residence time requires a reactor volume of 145 $m.^3$ for the bulk density of the material used in our experiments. The total reactor pressure which will be needed to maintain the 1 atm. hydrogen partial pressure is approximately 1.2 atm. for a hydrogen sulfide concentration in the product gas of 15 volume %. A summary of the unit costs for recovering the sulfur is given in Table I.

The cost of regenerating gas which completes the process cost items is not included in Table I because in a differential bed reactor conditions do not allow the extent of various side reactions which may consume hydrogen to be established. This data must be obtained in an integral reactor operating at gas conversion levels which are high enough to permit the extent of side reactions to be determined. Also, because of the kinetic similarity between the regeneration of seed–slag mixtures and alkalized alumina, it is reasonable to expect that a cheaper gas such as producer gas will be the regenerating gas in an actual plant.

Costs are not included for either recovering the seed from the combustion products or for recycling the seed to the MHD generator because these operations must be done whether the sulfur is recovered or not. Thus, sulfur recovery with an MHD-topped power plant will be much simpler than removing sulfur from conventional power stations.

**Table I. Unit Cost Per Day Including Taxes and Profit Based on 365 Days**

| | |
|---|---|
| Pelletizing | $ 128 (cost of pelletizing iron ore) |
| Seed–slag sulfur removal reactor | 639 (estimated from Katell, 1966) |
| Claus unit for converting $H_2S$ to S | 2300 (estimated from Graff, 1960) |
| Total unit cost | $3067 |

### *Conclusions*

Sulfur can be eliminated from the effluent gases of open-cycle MHD-topped power plants by recovering it from the recycling seed–slag mixture with hydrogen. The incorporation of this recovery step is a simple matter in the MHD-power station, because a potassium or cesium seeding material, which has a great affinity for sulfur, is added to make the combustion gas electrically conductive, and this seed must be recovered and recycled. Our kinetic model for the stripping of sulfur as hydrogen sulfide from seed–slag mixtures can be used to design reactors for this purpose. This model also describes the regeneration of the absorbent in the alkalized alumina process for removing sulfur dioxide from power plant stack gases.

### *Acknowledgment*

The authors express their appreciation to Raymond W. Hiteshue and Donald M. McCrea, Pittsburgh Coal Research Center, and Warren M. Mahan, Bureau of Mines, Hibbing, Minn., for providing some of the cost data and to Armido DiDonato of the Naval Weapons Laboratory, Dahlgren, Va., for testing the stability of the least-squares constants to errors in the rate measurements.

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# A Technique for Measuring Photochemical Reactions in Atmospheric Samples

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■ Photochemical experiments were conducted on samples collected from the atmosphere in downtown Los Angeles during the morning traffic peak hours. The samples were collected in large plastic containers, then subjected to reaction by solar radiation at ambient temperatures. Detailed compositional analyses were made for a number of inorganic and organic pollutants present as reactants and products. Results illustrate the utility of the technique for determining product yields and rates of reaction under realistic atmospheric conditions.

Although many photochemical studies have been carried out in the laboratory with mixtures that simulate reactive urban atmospheres, little work has been done with actual atmospheric samples. Synthetic mixtures of hydrocarbons and nitrogen oxides or diluted exhaust from an internal combustion engine are convenient, but these systems can only partially reproduce the conditions of atmospheric reaction. The Los Angeles atmosphere provides the best source of photochemically reactive samples.

Stephens and co-workers (Stephens and Burleson, 1967; Stephens, Darley, *et al.*, 1967) reported rates of reaction of aliphatic hydrocarbons in ultraviolet irradiation of atmospheric samples. In most of their experiments laboratory blacklight lamps were used to irradiate the atmospheric samples introduced into borosilicate glass carboys. Only a few experiments were performed with solar irradiation. Because the rigid containers hold only small samples, the analytical measurements were restricted to gas chromatographic analysis for hydrocarbons.

In the work reported here, large plastic containers fabricated from film transparent to solar radiation were used instead of smaller rigid containers. With the large, flexible containers, we performed much more complete analytical measurements similar to those usually applied to synthetic or automobile exhaust mixtures in very large (100 to 1000 ft.$^3$) laboratory irradiation chambers (Altshuller and Bufalini, 1965). This technique was tested with atmospheric samples collected in downtown Los Angeles during the morning traffic peak hours in October and November, 1967. With the large-size sample and a mobile laboratory nearby, analyses could be made for the following substances: aliphatic hydrocarbons, aromatic hydrocarbons, total hydrocarbon, nitric oxide, nitrogen dioxide, oxidant, formaldehyde, peroxyacetyl nitrate, and carbon monoxide. The results obtained during 6 days of experiments show the potential of this technique for evaluating the photochemical reactivity of urban atmospheres.

## *Experimental*

Plastic bags fabricated from Tedlar film (transparent to ground-level solar radiation) were filled with 150 l. of ambient air on the roof of the headquarters of the Los Angeles Air Pollution Control District. Samples were taken on the roof rather than near or at street level to avoid possible artifacts induced by local traffic conditions. The samples were collected between 7 and 8 a.m. Two bags were filled concurrently for each experiment. Particulates were not removed, since the intent was to utilize unmodified atmospheric samples. One sample was analyzed in the mobile laboratory, irradiated for 2 or 3 hr. with solar radiation at ambient temperatures, reanalyzed, irradiated again for 2 or 3 hr., and reanalyzed; in several experiments the samples were subjected to a third irradiation and a third analysis. The second sample from each experiment was analyzed, held in the dark for 3 hr., reanalyzed, held in the dark for another 3 hr., and analyzed again. This second series of measurements was made to determine the extent, if any, of homogeneous dark reactions, surface reactions, and surface adsorption. Such reactions would not be expected to be rapid, since oxidant and peroxyacetyl nitrate could not be detected at significant levels in the original samples and possible free-radical or other activated species would decay rapidly in the dark.

Trapping procedures were used to concentrate 75-cc. volumes of samples before analysis for either aliphatic or aromatic hydrocarbons. Details of the trapping techniques have been reported (Bellar, Brown, *et al.*, 1963; Lonneman, Bellar, *et al.*, 1968).

Aliphatic hydrocarbons were separated on a 21-ft. long, $^3/_{16}$-in. o.d. dibutylmaleate column, along with a 3-ft. length of bis-2(methoxyethyl)adipate. Aromatic hydrocarbons were separated on a 300-ft. long, 0.06-in. i.d. open tubular column coated with *m*-bis(*m*-phenoxy–phenoxy)benzene. Carbon monoxide was separated from methane on a molecular sieve column and hydrogenated to methane with Raney nickel on C-22 Celite catalyst. The hydrocarbons and carbon monoxide as well as methane were analyzed with a flame ionization detector. Peroxyacetyl nitrate was separated on a 9-ft. long, $^1/_8$-in. o.d. borosilicate glass column packed with 10% Carbowax 600 on 60–80 mesh Gas Chrom Z. Total hydrocarbons were determined with a flame ionization analyzer calibrated with propane. Methane was determined by use of a modified flame ionization analyzer with an activated carbon precolumn to hold back hydrocarbons other than methane (Altshuller, Ortman, *et al.*, 1966).

Concentrations were obtained for about 25 aliphatic hydrocarbons mostly in the two- to five-carbon range, but also including several six-carbon and higher paraffins. The concentrations of 16 to 18 of the seven- to ten-carbon alkylbenzenes were obtained concurrently. These hydrocarbons, along with methane, accounted, on the average, for 60% of the carbon measured by the total hydrocarbon analyzer. Much of the discrepancy was in the $C_6^+$ paraffin fraction not measured gas chromatographically in this study.

Oxidant, nitric oxide, nitrogen dioxide, and formaldehyde were analyzed by colorimetric techniques used previously (Altshuller, Kopczynski, *et al.*, 1967).

**Table I. Results and Analysis of Irradiated Samples**

| | | | Concentration, p.p.m. by volume | | | | |
|---|---|---|---|---|---|---|---|
| Date of experiment | Total hydrocarbon,[a] carbon p.p.m. | Methane,[a] carbon p.p.m. | Nitrogen[a] oxides | Carbon[a] monoxide | Maximum[b] formaldehyde | Maximum oxidant | Maximum peroxyacetyl nitrate |
| 10/12/67 | 16 | 4.5 | 0.95 | ... | 0.49 | 0.24 | 0.036 |
| 10/13/67 | 16 | 3.5 | 0.8 | ... | 0.13 | 0.18 | 0.027 |
| 10/20/67 | 20 | 5 | 1.15 | ... | 0.37 | 0.30 | 0.062 |
| 10/27/67 | 14 | 3.5 | 0.8 | ... | 0.31 | 0.25 | 0.043 |
| 11/13/67 | 10.5 | 4 | 1.1 | 23 | 0.19 | 0.26 | 0.026 |
| 11/14/67 | 9 | 4 | 1.0 | 20 | 0.16 | 0.25 | 0.046 |

[a] Initial concentration. From 9 to 40% of the $NO_x$ was in the form of nitrogen dioxide with an average of 26% of the initial content as nitrogen dioxide.

[b] Net formaldehyde produced by irradiation. The initial formaldehyde concentration before irradiation (0.1 p.p.m.) was subtracted from the total formaldehyde concentration after 6 hr.

*Results*

The analytical measurements (excluding detailed hydrocarbon analyses) are summarized in Table I. Oxidant levels during the 6 days of sampling were not extremely high for the Los Angeles Basin. Eye irritation was moderate to severe on several days, but very light on others. This sort of result is not unusual. Statistical relationships between oxidant and eye irritation are of limited applicability on a day-by-day basis. The ratios of total hydrocarbon to nitrogen oxide varied from 8:1 up to 20:1; these values are in the usual range (State of California, 1966). With methane excluded, the ratios varied from 5:1 to 16:1. If atmospheric organics are assigned an average carbon number of about 5, the molar ratio is in the 1:1 to 3:1 range. Values for both total hydrocarbon and nitrogen oxides obtained in this study were higher than the values obtained at the monitoring station of the Los Angeles County Air Pollution Control District on the floor below the rooftop sampling area. In part, the difference in hydrocarbon values results from the use of propane rather than methane as calibration gas. The differences between nitrogen oxide values can be attributed at least in part to the higher oxidation efficiency of the oxidant used in this study to convert nitric oxide to nitrogen dioxide.

Despite these differences, the maximum oxidant values obtained in this study agree reasonably well with those obtained at several air monitoring stations in the Los Angeles Basin (Table II).

Results obtained on October 20, 1967, are plotted in Figures 1 and 2 to illustrate in more detail the progress of an irradiation in the plastic container. As is usually observed in laboratory experiments, concentrations of oxidant and peroxyacetyl nitrate become detectable at about the time the nitrogen dioxide reaches its peak value and the nitric oxide has been reduced to a low value. As in all the experiments, formaldehyde is present initially because it comes from combustion sources; formation of formaldehyde continues through the irradiation period.

**Table II. Maximum Oxidant Concentrations Measured at Several Monitoring Stations (p.p.m. by volume)**

| Date of experiment | Bag irradiation | Downtown Los Angeles | Pasadena | Azusa |
|---|---|---|---|---|
| 10/12/67 | 0.24 | 0.21 | 0.29 | 0.32 |
| 10/13/67 | 0.18 | 0.25 | 0.33 | 0.29 |
| 10/20/67 | 0.30 | 0.24 | 0.33 | 0.50 |
| 10/27/67 | 0.25 | ND | 0.35 | 0.31 |
| 11/13/67 | 0.26 | 0.25 | 0.21 | 0.28 · |
| 11/14/67 | 0.25 | 0.25 | 0.26 | 0.27 |

As shown in Table I and Figure 1, the peroxyacetyl nitrate concentrations are always a small fraction of the oxidant values. The ratio of maximum oxidant to maximum peroxyacetyl nitrate varies from 5:1 to 10:1. The peroxyacetyl nitrate also accounts for no more than 5 or 6% of the nitrogen oxides consumed during the irradiation. Other peroxyacyl nitrates or alkyl nitrates do not appear to be significant products (Stephens and Darley, 1964; Stephens and Price, 1965). In the samples held in the dark, the average initial nitrogen oxide level of 98 p.p.hm. decreased over 6 hr. to 90 p.p.hm. This small decrease, probably due to loss to container walls, does not appreciably effect the material balance for nitrogen. These results support the conclusion from recent laboratory measurements (Bufalini and Gay, 1969) that a major part of the nitrogen oxide in the atmosphere is converted to nitric acid and particulate nitrate.

The decrease in oxidant in the latter stages of irradiation is also observed to a lesser extent in continuous laboratory irradiations of some types of hydrocarbon-nitrogen oxide mixtures. However, a portion of the decrease may be attributed to

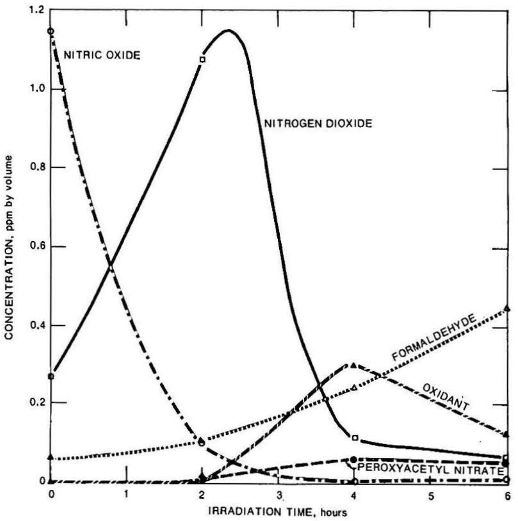

**Figure 1. Composition changes of nitric oxide and various products with irradiation time in atmospheric sample obtained October 20, 1967**

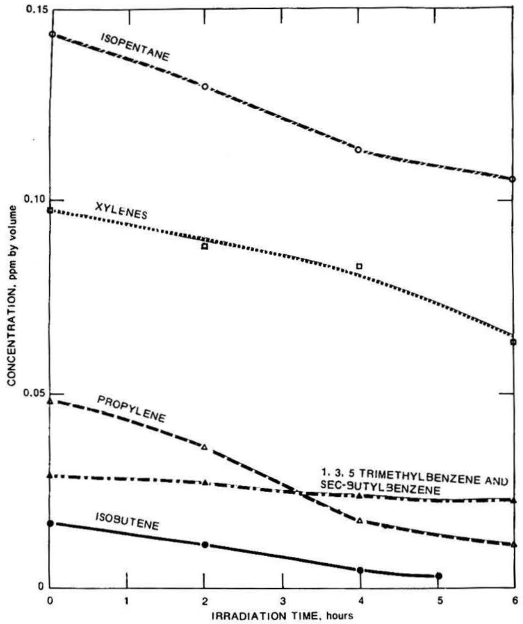

**Figure 2. Selected hydrocarbon consumption with irradiation time in atmospheric sample obtained October 20, 1967**

reaction of ozone with olefins in the dark periods during analysis. This aspect of the procedure needs improvement. It would also tend to increase the rate of conversion of some hydrocarbons, particularly of those olefins that react very rapidly with ozone, but would have little or no effect on the rates of conversion of alkylbenzenes and paraffins, which react extremely slowly with ozone at ambient concentrations.

Stability of individual aliphatic and aromatic hydrocarbons in the nonirradiated plastic containers over 6-hr. periods was very good. The concentration levels varied by no more than ±5%, with no significant trends. Most or all of the variability can be attributed to limitations in analytical precision in the sub-p.p.m. range. The hydrocarbon consumptions with time on one of the experiment days, October 20, 1967, are shown in Figure 2 for several aliphatic and aromatic hydrocarbons. Table III is a more detailed tabulation of hydrocarbon consumption based on the averaged results from experiments on the last 4 days, in which measurements were more complete; values are given for time to 10% consumption, $t_{0.10}$; 25% consumption, $t_{0.25}$; etc. Reactions of acetylene and propane were too slow to be detected within experimental precision. The consumption rates for *n*-butane and isobutane, although difficult to determine, appeared to be less than 10% in 6 hr. Pentane and isopentane definitely reacted to the extent of 10% conversion in 6 and 4 hr., respectively. Except for ethylene, the olefins reacted to 75% or more in 6 hr. The alkylbenzenes reacted at one-half to one-quarter the rate at which the three carbon and higher-molecular-weight olefins were consumed. Because of the higher concentrations of alkylbenzenes, particularly on a carbon-p.p.m. basis, almost exactly the same concentration of carbon atoms, 0.44 p.p.m., was consumed in reactions of alkylbenzenes as in reactions of olefins. The total carbon atoms consumed by reaction of olefins, acetylene, alkylbenzenes, and paraffins averaged 1.07 p.p.m. out of an average total carbon level (excluding methane) of 5.08 carbon p.p.m. Since the average yields of formaldehyde and peroxyacetyl nitrate from irradiation on the four experiment days were 0.26 and 0.09 carbon p.p.m., respectively, about 33% of the carbon atoms consumed could be accounted for as forming these two products.

The rates of consumption given in Figure 2 and Table III are based on experiments conducted between October 20 and November 14, 1967. By this time of the year the intensity of ultraviolet light has decreased from that available earlier in the fall and summer. Therefore, the conversion times earlier in the photochemical air pollution season should be shorter (rates higher) than those obtained in this study.

Stephens, Darley, *et al.* (1967) reported rates of consumption of several aliphatic hydrocarbons over an 8-hr. period using natural sunlight irradiation on one day, October 24, 1966. In the present study, as in this earlier experiment, acetylene reaction could not be detected and butanes reacted very slowly with natural sunlight. The reaction rates for the other paraffinic and olefinic hydrocarbons were reasonably consistent in the two studies and with the rankings of reactivities based on hydrocarbon rates of reaction reported in laboratory studies (Altshuller, 1966). No marked synergistic effects on rates of hydrocarbon reaction were observed in comparing irradiation of these complex atmospheric hydrocarbon mixtures with the laboratory irradiations of single hydrocarbons with nitrogen oxides.

This investigation clearly indicates the value of large plastic reaction containers in investigating the kinetic behavior of atmospheric samples at ambient temperatures with solar radiation. The useful results of this work should encourage others to conduct such investigations of compositional changes under actual atmospheric conditions.

These measurements form one class of information needed to quantitate our knowledge of reactions in urban atmospheres. Such measurements deliberately isolate the reaction mixtures from variations in source strength and changes in atmospheric ventilation as irradiation proceeds. Aerometric measurements of samples obtained at ground level and aloft, subjected to variations in both kinetic and meteorological factors, also are needed and are being obtained.

**Table III. Consumption Times for Hydrocarbons in Atmospheric Samples Subjected to Solar Irradiations**

| | Time for fractional conversion,[a] hr. | | | | |
|---|---|---|---|---|---|
| Hydrocarbon | $t_{0.10}$ | $t_{0.25}$ | $t_{0.50}$ | $t_{0.75}$ | $t_{0.90}$ |
| *n*-pentane | 6 | | | | |
| isopentane | 4 | | | | |
| propylene | 1 | 2 | 3.5 | 6 | |
| 1-butene + isobutene | 1 | 2 | 3.5 | 6 | |
| *cis*- or *trans*-2-butene | | | | | less than 2 |
| 1,3-butadiene | 0.5 | 1 | 2 | 4 | |
| 1-pentane | | | 3 | | 6 |
| *cis*-2-pentene | | | | | less than 2 |
| 2-methyl-1-butene | | | | | 4 |
| 2-methyl-2-butene | | | | | less than 2 |
| toluene | 6 | | | | |
| *p*-xylene | 3 | 6 | | | |
| *o*-xylene | 3 | 6 | | | |
| *m*-xylene | 2 | 4 | | | |
| *m* and *p*-ethyltoluene | 2 | 5 | | | |
| *sec*-butylbenzene + 1,3,5-trimethylbenzene | 3 | 4 | | | |
| 1,2,4-trimethylbenzene | | 3 | | | |

[a] Conversion times obtained from averaged results from four experiment days in October and November, 1967.

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# Singlet Oxygen in the Environmental Sciences. VIII. Production of $O_2(^1\Delta_g)$ by Energy Transfer from Excited Benzaldehyde under Simulated Atmospheric Conditions

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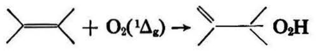
■ The production of singlet molecular oxygen *via* the absorption of light (λ > 2900 Å) by benzaldehyde and subsequent energy transfer to ground state molecular oxygen has been observed under simulated atmospheric conditions. The singlet oxygen was detected by monitoring the hydroperoxide product of its reaction with 2,3-dimethyl-butene-2 by long path length ir spectroscopy. Other mechanisms for hydroperoxide formation in the system are discussed. These are direct absorption of visible radiation by ground state oxygen to give $O_2(^1\Sigma_g^+)$ which is collisionally deactivated to $O_2(^1\Delta_g)$, and secondly, absorption of uv light by an oxygen-olefin "collision complex." This may lead directly to the hydroperoxide product or result in the perturbation and enhancement of the "forbidden" singlet-triplet absorption of 2,3-dimethyl-butene-2 by $O_2(^3\Sigma_g^-)$ followed by energy transfer to give hydroperoxide.

Recently, the possible role of singlet molecular oxygen, $O_2(^1\Sigma_g^+$ or $^1\Delta_g)$, in the photochemistry of polluted urban atmospheres of the Los Angeles type has attracted much attention (Pitts, 1969; Kummler, Bortner, *et al.*, 1969). Pitts, Khan, *et al.* (1969) have proposed that $^1O_2$ may be formed in polluted urban atmospheres by (i) direct absorption of solar radiation by ground state molecular oxygen, $O_2(^3\Sigma_g^-)$, (ii) absorption of solar radiation by organic pollutant molecules and subsequent transfer of energy to ground state molecular oxygen, (iii) photodecomposition of ozone, and (iv) as a product of exothermic chemical reactions.

Kummler and Bortner (1969) observed the 1.27 μ emission of $O_2(^1\Delta_g)$ when they irradiated mixtures of benzaldehyde and oxygen with the unfiltered output of a 500 watt Hg-Xe arc lamp. By our research we hoped to show experimentally that route (ii) above is feasible, under pseudoatmospheric conditions, using benzaldehyde as a sensitizer.

Broadbent, Gleason, *et al.* (1968) have shown that 2,3-dimethyl-butene-2 (DMB) reacts rapidly and almost quantitatively with $O_2(^1\Delta_g)$ to give 2,3-dimethyl-3-hydroperoxybutene-1


(1)

The hydroperoxide has characteristic ir absorption bands at 3594 and 906 cm.$^{-1}$ (Broadbent, Gleason, *et al.*, 1969) which are not masked by absorptions of the parent DMB. We hoped to sensitize the formation of $^1O_2$ by the Kautsky (1939) mechanism under simulated atmospheric conditions, trap the singlet oxygen by Reaction 1 and follow the hydroperoxide formation by monitoring the ir absorptions at 3594 and 906 cm.$^{-1}$ The mechanism would be

$$B(S_o) + h\nu \rightarrow B(S_1) \quad (2)$$

$$B(S_1) \xrightarrow{\text{inter-system crossing}} B(T_1) \quad (3)$$

$$B(T_1) + O_2(^3\Sigma_g^-) \rightarrow B(S_o) + {}^1O_2(^1\Sigma_g^+ \text{ or } ^1\Delta_g) \quad (4)$$

followed by Equation 1. *B* represents benzaldehyde and $S_o$, $S_1$, and $T_1$ are its ground, and first excited singlet states, and first excited triplet state, respectively.

**Experimental.** The apparatus consisted of a conventional high vacuum gas handling system connected to the 40 m. path length cells of a modified Perkin Elmer 621 ir spectrophotometer (Figure 1). The whole system could be evacuated to ~$10^{-5}$ torr.

Six 7 × 6 cm. quartz windows in the sample cell allowed the contents to be irradiated perpendicular to the ir analyzing beam. The light source was an Hanovia 1200-watt medium pressure Hg lamp housed in a hollow quartz jacket. Either

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distilled water, copper sulfate solution (30 g. $CuSO_4 \cdot 5H_2O$/100 ml. $H_2O$) or potassium dichromate (10 g. $K_2Cr_2O_7$/100 ml. $H_2O$) was flowed through this jacket and acted as a light filter and lamp coolant. The lamp output was also always filtered by 2-mm. borosilicate glass plates over the cell windows. The band passes of these filters are shown in Figure 2. The emission spectrum of the lamp is similar to that given by Calvert and Pitts (1966).

**Materials.** 2,3-Dimethyl-butene-2 (DMB) (either Chemical Samples Co., J. T. Baker Chemical Co., or Chemical Procurement Laboratories, Inc.) and benzaldehyde (Matheson, Coleman, and Bell, "chlorine-free grade") were purified by two bulb-to-bulb distillations and middle cuts stored in darkened side arms at −196° C. Both compounds were pure by ir. 2,3-Dimethyl-3-hydroperoxybutene-1 was prepared in our laboratories by Mr. J. Hughes using the rose bengal photosensitized oxidation of DMB (Schenk and Schulte-Elte, 1958). The sample used was better than 97.5% pure. Laboratory air was filtered and dried (Matheson Co., type "a" gas purifier) and then passed through a 50-cm. column of anhydrous $CaSO_4$ into the reaction cells. No water could be detected in this air by long path length ir. Air zero gas (Azg) (Matheson Gas Products) and oxygen (Matheson Gas Products, ultrahigh purity grade) were used without further purification.

**Procedure.** Benzaldehyde was expanded into the sample cell from a known volume, followed by DMB. Air or oxygen was then bled in to give 700 torr pressure and the reactants allowed to mix. The sample cell was opened to the reference cell and the mixture equilibrated. The reference cell was then isolated and air (or oxygen) bled into the sample cell to give a total pressure of 700 torr. The mixture was then irradiated and simultaneously analyzed by ir. A "null" method of analysis was used. The absorptions by the equal amounts of benzaldehyde and DMB in the sample and reference cells cancel and only absorptions due to reaction products appear on the recorder.

All experiments were performed at 24 ± 1° C. The conversion of DMB was less than 1% in all experiments.

### *Results and Discussion*

Preliminary experiments were carried out using distilled water as coolant in the lamp jacket. A mixture of 2.5 p.p.m. benzaldehyde and 640 p.p.m. DMB in 700 torr dried laboratory air was irradiated for 4500 sec. and the transmissions at 3594 and 906 $cm.^{-1}$ monitored at 200-second intervals using the recorder's (×20) ordinate expansion. Absorption increased at both frequencies during irradiation and did not decrease when the lamp was switched off. The ratio of the extinction coefficients of the two absorptions was 3.2. This is in good agreement with the value of 3.1 obtained by Broadbent, Gleason, *et al.* (1969) and is good evidence that we were observing hydroperoxide formation.

The rate of production of hydroperoxide was calculated from the least-squares slope (with 95% confidence limits) of a plot of log $I_0/I_T$ (3594 $cm.^{-1}$) against time using the decadic extinction coefficient, $\epsilon$ = 3.21 1 $cm.^{-1}$ $mole^{-1}$ measured in our apparatus. For this run, the rate of hydroperoxide formation ($R_p$) was 1050 ± 110 p.p.hm. $hr.^{-1}$

Blank experiments were carried out in which one of the reactants, either benzaldehyde, DMB, or dried laboratory air, was absent. No hydroperoxide was formed without irradiation or when mixtures of benzaldehyde and DMB were irradiated. However, irradiation of 640 p.p.m. DMB in the presence of 700 torr air gave hydroperoxide with $R_p$ = 960 ± 220 p.p.hm. $hr.^{-1}$ [It has been suggested that the hydroperoxide product might be formed by a free radical attack on the DMB rather than by singlet oxygen. As yet, we have found no evidence for free radical processes, but are further investigating this possibility.]

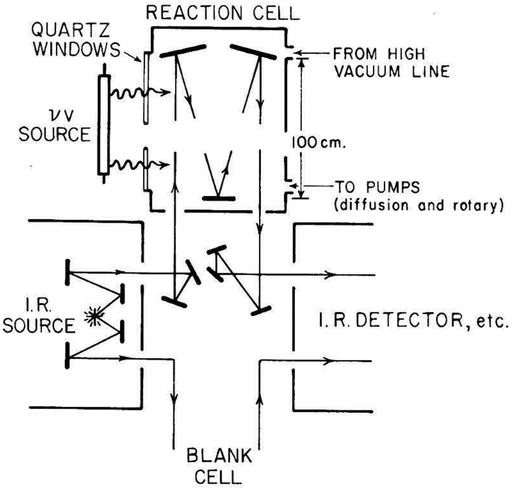


**Figure 1. Diagram of the long path length ir apparatus**

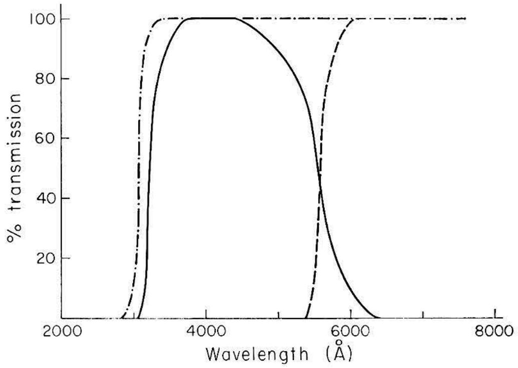


**Figure 2. Band passes of filters**

**–·–·– borosilicate glass (2 mm. thickness); —— 30 g. $CuSO_4 \cdot 5H_2O$/100 ml. $H_2O$, 1 cm. thickness; – – – 10 g. $K_2Cr_2O_7$/100 ml. $H_2O$, 1 cm. thickness**

At first, we suspected that an impurity in the dried laboratory air was causing this hydroperoxide formation. When 640 p.p.m. DMB was irradiated in the presence of 700 torr Azg, and when 0.45 torr DMB was irradiated in the presence of 140 torr of ultrahigh purity oxygen (these are equivalent to the DMB and oxygen pressures in the air experiments), then we obtained $R_p$ = 970 ± 200 and 1070 ± 210 p.p.hm.-$hr.^{-1}$, respectively. It seems unlikely that an impurity would be present at the same concentration in three such widely different sources of oxygen.

DMB from two additional suppliers was irradiated in the presence of 700 torr Azg. $R_p$ for both agreed within experimental error. The possibility that the reaction vessel walls were sensitizing the hydroperoxide formation was checked. The cell was dismantled, thoroughly cleaned, and the cell and optical bench lined with aluminum foil. An experiment immediately before dismantling gave $R_p$ = 1110 + 270 p.p.hm. $hr.^{-1}$, and one directly after reassembly, $R_p$ = 1170 + 160 p.p.hm. $hr.^{-1}$ All the remaining experiments were carried out in the Al foil lined cell.

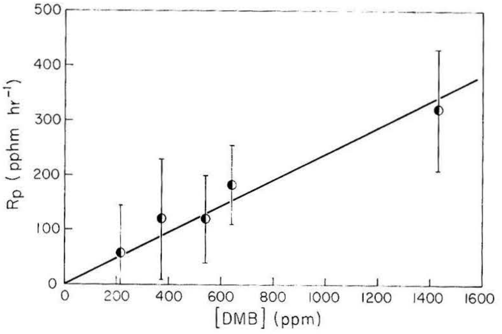


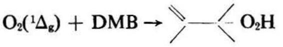
**Figure 3. Variation of the rate of hydroperoxide formation with (DMB) using dichromate filtered light**

The effect of the wavelength of irradiation upon $R_p$ was investigated using $CuSO_4$ and $K_2Cr_2O_7$ solutions as filters. With the dichromate filter, irradiation of 0.45 torr DMB in the presence of 140 torr ultrahigh purity oxygen gave $R_p = 185 \pm 141$ p.p.hm. hr.$^{-1}$ Irradiating a similar mixture using the $CuSO_4$ filter solution gave $R_p = 440 \pm 141$ p.p.hm. hr.$^{-1}$

Examination of Fig. 2 shows that with the dichromate filter, light will be absorbed by the red atmospheric system of oxygen, $O_2(^1\Sigma_g^+) \leftarrow O_2(^3\Sigma_g^-)$, between 5700 and 7700 Å (Cho, Allin, *et al.*, 1963). Thus, hydroperoxide is probably formed by the mechanism

$$O_2(^3\Sigma_g^-) + h\nu \rightarrow O_2(^1\Sigma_g^+) \qquad (5)$$

$$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^1\Delta_g) + M \qquad (6)$$



$$O_2(^1\Delta_g) + \mathrm{DMB} \rightarrow \quad O_2H \qquad (1)$$

where $M$ is some deactivating molecule. This is route (i) for singlet oxygen production mentioned in the introduction. A number of experiments were carried out where 214–1428 p.p.m. DMB in 700 torr Azg were irradiated with the dichromate filtered light. A plot of $R_p$ against (DMB) is shown in Figure 3. A least-squares treatment of the results gave

$$R_p = (0.24 \pm 0.12)\ (\mathrm{DMB})\ \text{p.p.m. hr.}^{-1} \qquad (7)$$

The units of (DMB) are p.p.m. and the errors quoted here and elsewhere in the paper are the 95% confidence limits.

Interpretation of the result with the copper sulfate filter solution is more difficult. The uv vapor phase spectra of DMB, Azg, ultrahigh purity oxygen, and a mixture of DMB and Azg were measured with a Cary 15 uv spectrophotometer. No spectrum showed any absorption between 2900 and 6700 Å (the latter is the long wavelength cutoff for the sulfate filter). Although the sulfate filter passes some light which can be absorbed by the oxygen's red atmospheric system, the whole system can absorb when the dichromate filter is used. Therefore, it is unreasonable that $R_p(CuSO_4) > R_p(K_2Cr_2O_7)$ if the rate difference is due to attenuation of the wavelengths available for Reaction 5. The reason for the difference in rates must stem from the different short wavelength cutoffs for the sulfate solution and Pyrex filters.

Hoijtink (1969) has recently reviewed singlet-triplet absorptions induced by paramagnetic perturbers such as oxygen. The mechanism involves the formation of a collision complex, with overall triplet character, between ground state molecular oxygen and DMB and includes enhancement of the "forbidden" singlet-triplet absorption of DMB. Subsequently several paths may lead to formation of the hydroperoxide, for example,

$$^3O_2 + {}^1\mathrm{DMB} \underset{b}{\overset{a}{\rightleftarrows}} {}^3(^3O_2 + {}^1\mathrm{DMB}) \qquad (8)$$

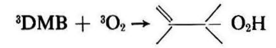
This may absorb light

$$^3(^3O_2 + {}^1\mathrm{DMB}) + h\nu \rightarrow {}^3(^3O_2 + {}^3\mathrm{DMB}) \qquad (9)$$

and dissociate to give ground state molecular oxygen and the first excited triplet state of DMB,

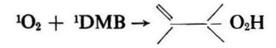
$$^3(^3O_2 + {}^3\mathrm{DMB}) \rightarrow {}^3O_2 + {}^3\mathrm{DMB} \qquad (10)$$

The energy of the first excited triplet state of DMB has not been measured. However, Evans (1959) has proposed that the triplet energy of ethylene is ~82 kcal. mole$^{-1}$ and Cundall and Griffiths (1965) have argued that a reasonable value for 2-butene is ~70 kcal. mole$^{-1}$. Light of wavelength 4000 Å has an energy of 71.5 kcal. mole$^{-1}$. By comparison to the oxygen perturbed spectrum of benzene (Evans, 1957) one would expect the complex formed in Reaction 8 to start absorbing near 4000 Å. This absorption will probably increase toward shorter wavelengths and a higher extinction coefficient would be expected at 2900 Å compared to 3100 Å. This is the region of the spectrum which we feel is responsible for the above results. Reactions 8–10 could be followed by



$$^3\mathrm{DMB} + {}^3O_2 \rightarrow \quad O_2H \qquad (11)$$

$$^3\mathrm{DMB} + {}^3O_2 \rightarrow {}^1\mathrm{DMB} + {}^1O_2 \qquad (12)$$



$$^1O_2 + {}^1\mathrm{DMB} \rightarrow \quad O_2H \qquad (1)$$

and an alternative reaction for the deactivation of $^1O_2$

$$^1O_2 + {}^3O_2 \rightarrow 2\,{}^3O_2 \qquad (13)$$

The reaction

$$^1O_2 + N_2 \rightarrow {}^3O_2 + N_2$$

need not be considered. Steer, Pitts, *et al.* (1969); Findlay, Fortin, *et al.* (1969); and Clark and Wayne (1969) have shown that under atmospheric conditions the rate of this reaction is ~300 times slower than that of Reaction 13. The absence of an observable absorption in the 2900–4000 Å region of the uv spectrum of the DMB/Azg mixture does not disqualify this mechanism. Such perturbed absorptions are weak; for benzene, oxygen pressures ~2000 p.s.i. are required to examine the "forbidden" singlet-triplet absorption (Evans, 1957).

A steady-state treatment of Reactions 1, 8–13 gives

$$R_p = \frac{k_a k_9(\mathrm{DMB})(O_2)}{(k_{8a} + k_9)(k_{11} + k_{12})} \left\{ k_{11} + \frac{k_{12}}{1 + \dfrac{k_{13}(O_2)}{k_1(\mathrm{DMB})}} \right\} \qquad (14)$$

A series of runs was carried out in which 86–650 p.p.m. DMB were irradiated in the presence of 700 torr Azg using the borosilicate glass filters. A plot of $R_p$ against (DMB) was a straight line (Figure 4). A least-squares treatment of the results gave

$$R_p = (1.71 \pm 0.11)\ (\mathrm{DMB})\ \text{p.p.hm. hr.}^{-1} \qquad (15)$$

where the units of (DMB) are p.p.m. The results of experiments where 0.45 torr DMB and varying pressures of oxygen were irradiated also gave a straight line plot of $R_p$ against $(O_2)$. Equation 14 would predict this if either $k_{11} \gg k_{12}$ or $k_1$ (DMB) was considerably greater than $k_{13}(O_2)$. There is no value in the literature for either $k_{11}$ or $k_{12}$. Steer, Pitts, *et al.* (1969) have found that $k_{13} = (1.23 \pm 0.14) \times 10^3$ mole$^{-1}$ sec.$^{-1}$ There are two values for $k_1$. Ogryzlo, *et al.* (1968) have estimated that $k_1 = 10^8$ mole$^{-1}$ sec.$^{-1}$ While preliminary results of Steer and Pitts (1969) indicate that $k_1 = (7.38 \pm 0.40) \times 10^5$ mole$^{-1}$ sec.$^{-1}$ If Ogryzlo's figure is correct, then in our experiments where $(O_2) \sim 10^3$ (DMB) a plot of $R_p$ against (DMB) would be a straight line regardless of the values of $k_{11}$ and $k_{12}$. However, if we accept Steer and Pitts' value, then the mechanism predicts straight lines only if $k_{11} \gg k_{12}$. Obviously, proof of the mechanism must await accurate measurement of $k_1$, $k_{11}$ and $k_{12}$.

Although the mechanisms which lead to hydroperoxide formation when mixtures of DMB and Azg are irradiated are not unambiguously established, the values of $R_p$ obtained were reproducible. Thus, a series of experiments were performed with varying concentrations of benzaldehyde (3–43 p.p.m.) and 640 p.p.m. DMB in 700 torr Azg. A plot of $R_p$ against (benzaldehyde) is shown in Figure 5. A least-squares treatment of the results gave

$$R_p = (10.30 \pm 1.10) + (0.06 \pm 0.05) \text{ (benzaldehyde) p.p.m. hr.}^{-1} \quad (16)$$

where the units of (benzaldehyde) are p.p.m. The intercept of Equation 16 represents $R_p$ for 640 p.p.m. DMB and 700 torr Azg and is in excellent agreement with the value of $R_p = 10.94 \pm 0.70$ p.p.m. hr.$^{-1}$ from Equation 15 for mixtures of DMB and Azg. The slope portion of Equation 16 represents the rate of the benzaldehyde sensitized formation of hydroperoxide (Reactions 1–4 and 13) and is

$$R_p = (6 \pm 5) \text{ (benzaldehyde) p.p.hm. hr.}^{-1} \quad (17)$$

where the units of (benzaldehyde) are p.p.m.

The data of Equations 7, 15, and 17 may be used to estimate the rates of hydroperoxide formation in our apparatus at atmospheric concentrations of DMB and benzaldehyde. If one assumes concentrations of 0.5 p.p.m. for these compounds, then for the direct absorption of radiation by oxygen, from Equation 7

$$R_p = 0.12 \pm 0.12 \text{ p.p.hm. hr.}^{-1}$$

For the oxygen perturbed mechanism, Reactions 1, 8 through 13, Equation 15 predicts that

$$R_p = 0.85 \pm 0.11 \text{ p.p.hm. hr.}^{-1}$$

Extrapolation of the rate of benzaldehyde sensitized formation of hydroperoxide to 0.5 p.p.m. DMB and benzaldehyde is not possible using our data. However, Equation 17 predicts that

$$R_p = 3.0 \pm 5.0 \text{ p.p.hm. hr.}^{-1}$$

for 0.5 p.p.m. benzaldehyde and 640 p.p.m. DMB. These rates do not represent the rate of production of singlet oxygen. Some $^1O_2$ will be deactivated by Reaction 13 but estimation of the amount must await accurate determination of $k_1$.

The results show that benzaldehyde does sensitize the formation of $O_2(^1\Delta_g)$ under pseudoatmospheric conditions, albeit at a rather slow rate. This may be partly due to the ease with which benzaldehyde is oxidized to benzoic acid by ground state molecular oxygen. Such a reaction would compete directly with Reaction 2 and decrease the concentration of benzaldehyde. This complication will not occur with other sensitizers such as acrolein (Marsh and Pitts, 1969) which is highly resistant to photooxidation (Osborne, Pitts, *et al.*, 1962) and photodecomposition (Coomber and Pitts, 1969).

The formation of hydroperoxide *via* Reactions 1, 8–12 is interesting. The vapor phase uv spectrum of 2,3-dimethyl-3-hydroperoxy-butene-1 was measured and showed a continuous

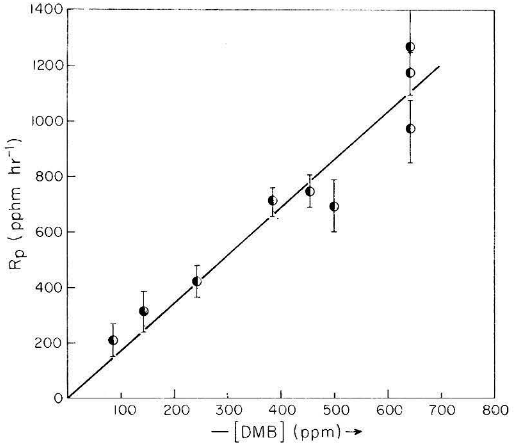


**Figure 4. Variation of the rate of hydroperoxide formation with (DMB) using Pyrex filtered light**

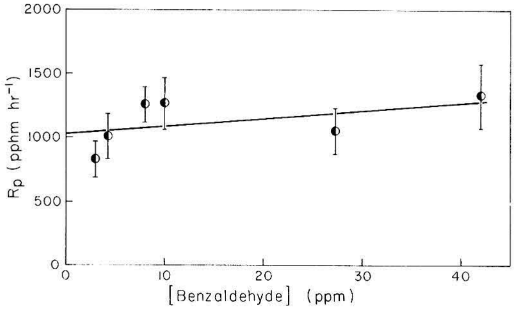
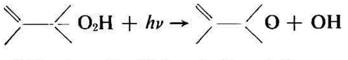


**Figure 5. Variation of the rate of hydroperoxide formation when varying benzaldehyde concentrations and 640 p.p.m. DMB are irradiated in the presence of 700 torr Azg**

and decreasing absorption from 2100–3100 Å. The hydroperoxide probably photodecomposes according to Reaction 18 (Calvert and Pitts, 1966)

 (18)

Because of the low O—O bond dissociation energy of the hydroperoxide, the radicals produced will probably carry a considerable amount of excess energy. The reactions of alkoxyl and hydroxyl radicals in polluted atmospheres have been discussed by Leighton (1961). The reaction between $OH + CO \rightarrow CO_2 + H$ is an intriguing, possible atmospheric process that has recently been proposed by several investigators.

Great caution should be exercised in extrapolating this data to actual atmospheric conditions. One difficulty is that our lamp has a banded emission spectrum whereas solar radiation is a continuum crossed by the Fraunhofer lines. The output of our lamp at 3130 Å is ~3000 μwatts cm.$^{-2}$ and at 5780 Å, ~4000 μwatts cm.$^{-2}$ For solar radiation in the lower atmosphere the figures are ~800 μwatts cm.$^{-2}$ and 1800 μwatts cm.$^{-2}$ for 100 Å bands centered at 3100 and 5750 Å, respectively. Secondly, we have a static experimental system whereas in urban atmospheres the primary pollutants (NO, hydrocarbons, etc.) are continuously replenished throughout the reaction. However, with these reservations, it appears that the formation of singlet molecular oxygen in polluted urban atmospheres *via* absorption of light by organic pollutant molecules and subsequent transfer of energy to ground state molecular oxygen is possible.

### *Acknowledgment*

We wish to thank D. G. Marsh and R. P. Steer for many helpful discussions. This work was supported by Grant AP 00109, Research Grants Branch, National Air Pollution Control Administration, Consumer Protection and Environmental Health Service, U.S. Public Health Service.

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# Bimetallic Coalescers: Electrophoretic Coalescence of Emulsions in Beds of Mixed Metal Granules

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■ Rapid coalescence of dilute oil-in-water or water-in-oil emulsions has been obtained by passing these through beds containing a granular mixture of dissimilar metals (such as iron and aluminum) or of carbon with a metal. Complete coalescence of dilute (*e.g.,* 0.1%) emulsions has been obtained with average residence times as short as 5 sec. Preliminary indications are that the efficiency of these coalescers often increases when the emulsion is more dilute, so that the cleanup of last traces of suspended droplets becomes easy.

Modern industrial and municipal waste treatment requires faster and more economical methods for coalescing dilute suspensions or emulsions. Increasingly severe pollution control standards are beginning to dictate expenditures in the millions of dollars to eliminate suspended oil or chemicals from waste water. Rapid coalescence is also needed in some water-in-oil suspensions. Suspended water in jet fuels is of major concern; accidental traces of surface-active materials in jet fuel inactivate the normal filter-coalescers so that suspended water is carried all the way to the field, where it provides a potential hazard to aircraft. Suspended water is also a problem in other fuels, oil products, and chemicals. The removal of catalysts from polymer solutions in the production of stereospecific rubbers or adhesives often involves some difficulty in removing finely divided droplets of wash solution.

The novel coalescing system described herein has shown promise of rapid and economical coalescing of the above-mentioned systems, but no complete engineering assessment of its potentialities has as yet been reported.

In a basic study of suspended particles in oil it was observed that positively charged particles plate out onto iron in contact with aluminum. This was postulated to result from interaction of the particles with the electrical field of the iron-aluminum couple in which the iron is negatively charged. Such an effect was observed in a beaker test as sketched in Figure 1. Application of this principle to the coalescence of suspended liquids or solids was then tried by passing a stream of the suspension through a bed of mixed metal granules, as shown in Figure 2 (initially aluminum and iron); the success of these tests led to this coalescence study.

## *Experimental*

Various bimetal and carbon-metal beds were tested for ability to coalesce oil-in-water (O/W) and water-in-oil (W/O) emulsions. The emulsions were percolated through the mixed-bed column and effluent collected in fractions. Figure 3 is a photograph of a column packed with carbon (4–8-mesh) and aluminum (20-mesh). The visible inhomogeneity of the column, due to the disparate particle size and density of the

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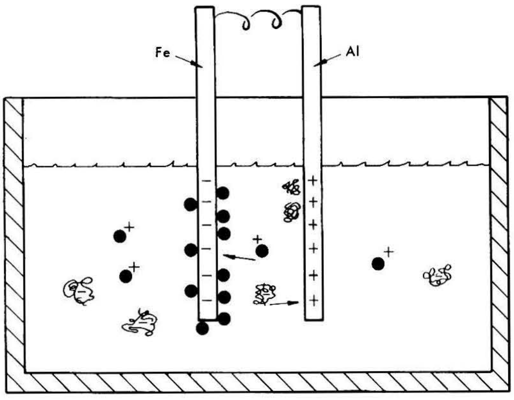

Figure 1. Electrodeposition of positively charged particles on the cathode of a bimetallic couple

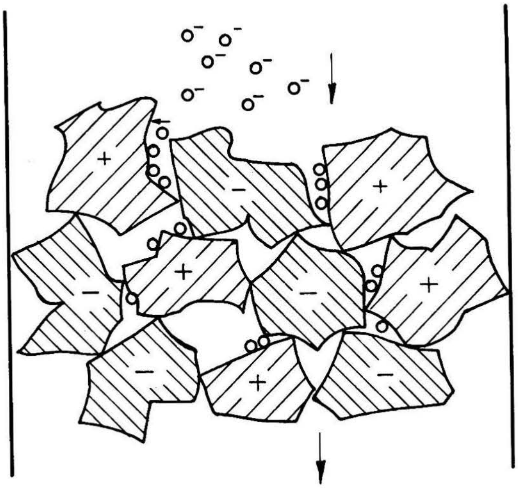

Figure 2. Diagram of granules in beds of bimetallic coalescers

two components, did not prevent the column from functioning as a coalescer. In Figure 4 the right-hand tube shows the clarity of the effluent obtained using an O/W emulsion from a distillation column of an oil refinery as feed to the column. The left-hand and center tubes contain effluent from a carbon and an aluminum bed, respectively. Figure 5 shows, from left to right, tubes of effluent collected when the same O/W emulsion as above was percolated through carbon, iron, and mixed carbon–iron beds, respectively. The slight, dark solid phase at the bottom of the right-hand tube is ferric hydroxide formed by hydrolysis of iron sacrificed to the effluent in the electrolysis at the iron surface. Table I lists the effluent oil content after passage of the same O/W emulsion (1100 p.p.m. oil) through various mixed beds.

From the photographs and the data in Table I, it is apparent that carbon in combination with either aluminum or iron effectively removed low concentrations of oil from this O/W emulsion. Thus, the method has distinct potentialities for purification of oil-polluted water from refinery operations.

Similar success was obtained in the treatment of W/O emulsions. Water haze produced during catalyst extraction was removed from hexane solutions of ethylene–propylene copolymer. The effluent was clear and bright and contained no water droplets when examined by optical microscopy.

Another W/O emulsion, 1000 p.p.m. water in kerosene, also responded nicely to the mixed-bed treatment, the kerosene having a water content of approximately 50 p.p.m. after passage through a carbon–iron column.

Figure 6 shows light transmission results obtained with a 1000-p.p.m. haze of water in 640 aviation kerosene, with various surface-active agents added at 50 p.p.m. to stabilize the haze. With a polymeric dispersant (Alkadine) which gives water droplets a negative charge, concentrations of both 50 and 10 p.p.m. were used. The faster coalescence with 10 p.p.m. is believed to result from the greater zeta-potential in dilute solutions. The dashed line is calculated from the 10 p.p.m. line, using the prediction that the zeta-potential should be inversely proportional to the square root of the concentration.

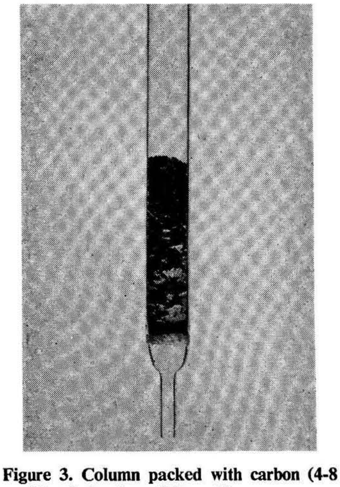

Figure 3. Column packed with carbon (4-8 mesh) and aluminum (20-mesh)

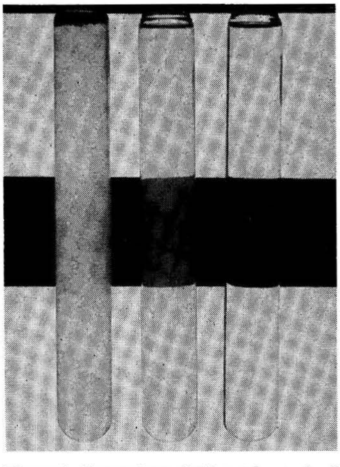

Figure 4. Comparison of effluent from mixed carbon/aluminum bed (right-hand tube) with effluents from beds of carbon (left) and aluminum (center)

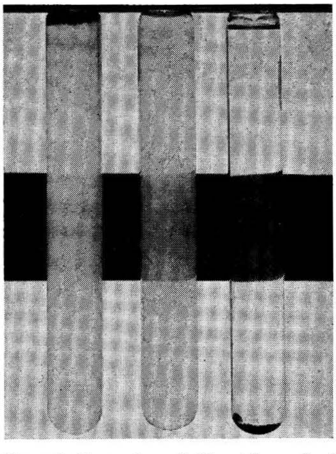

Figure 5. Comparison of effluent from mixed carbon/iron (right) with effluents from beds of carbon (left) and iron (center)

The rates of coalescence can be calculated from the light transmission data shown in Figure 6. The transmission coefficient is

$$I/I_o = e^{-k_1cl}$$

where $I$ is the intensity of transmitted light, $I_o$ is the light transmission of the solvent, $k_1$ is a constant, $c$ is droplet concentration, $l$ the length of cell. The equations for the straight lines of Figure 6 are of the form

$$I/I_o = b + k_2t_r = e^{-k_1cl}$$

where $b$ is the transmission coefficient of the initial suspension, $k_2$ is the slope of the line, and $t_r$ is the residence time. The rate of coalescence ($-dc/dt_r$) is therefore:

$$\frac{-dc}{dt_r} = \frac{k_2}{k_1l(k_2t_r + b)}$$

The rate of coalescence is seen to decrease as residence time increases, and is found to be proportional to the concentration of droplets. That is, first-order kinetics prevail. Thus, for any of the curves in Figure 6, the number of droplets coalesced per second is a constant fraction of the total number present, but the fraction is far greater for emulsions with a sulfonate surfactant than with the polymeric surfactant (Alkadine).

### *Discussion*

**Basic Principle.** In both water-in-oil and oil-in-water emulsions, the droplets are very often electrically charged with respect to the continuous phase and in an electric field tend to move toward the electrode of opposite charge. On close approach to the electrode, the droplets are coalesced and largely discharged.

The rate of movement of spherical particles in an electric field ($v$, electrophoretic velocity) is a function of the potential difference between the moving droplets and the surrounding liquid, $\zeta$ (the zeta-potential) and the viscosity, $\eta$, of the liquid

$$v = \frac{\zeta EK}{6\pi\eta}C$$

where $E$ is the electric field in V per cm., $K$ the dielectric constant, and where $C$ varies from 1.0 to 1.5, depending on whether the effective hydrodynamic radius is determined mainly by the particle or mainly by the attending ionic atmosphere (Henry, 1931).

In most stable emulsions, the value of the zeta-potential is 25 mV or greater, and consequently in light hydrocarbons electrophoretic velocities are on the order of $0.2 \times 10^{-4}$ cm. per sec. in a field of 1 V per cm. In water, $K$ (and therefore $v$) is about 40 times greater.

If two metals differing by 1 V in electromotive potential are connected by a good conductor, electrons flow from the less noble to the more noble metal (*e.g.*, from aluminum to iron) until the Fermi levels are equal and a contact potential difference of about 1 V is established between the two. If such a system is immersed in an emulsion or suspension as shown in Figure 1, the resulting electric field causes charged droplets or particles to deposit on one of the electrodes (Koelmans and Overbeek, 1954) (*e.g.*, positively charged bodies plate out on the iron and negatively charged bodies plate out on the aluminum). If the emulsion is much less conductive than the connection between the two electrodes, virtually all of the potential drop occurs through the emulsion; this is the desired situation for maximum efficiency in coalescence. The composition of electrodes, geometry of the bed, and the surface conductance can be important in determining conductance in the bed.

In beds of mixed metal granules, the electric field in the emulsion between granules depends on the distance of separation (Figure 2). A separation of $10^{-2}$ cm. between granules having a potential difference of one V gives an electric field of 100 V per cm. In this field, emulsion droplets having an electrophoretic velocity of $10^{-4}$ cm. per sec. per V per cm. would be all plated out in 1 sec. Of course, in such beds the differences in the distance separating adjacent particles varies widely; in some parts of the bed the electric field may be only 10 V per cm. and in others greater than 1000 V per cm. The choice of shape and size of granules can determine the average separation, and therefore the average field strength.

### *Choice of Metals*

The choice of metals is important in such coalescers. Obviously, large potential differences are desirable and examination of the electromotive series of metals suggests reactive metals, such as magnesium or aluminum, in combination with noble metals, such as gold. These give potential differences of about 3 V. Carbon is far more practical than gold, takes the role of a fairly noble metal, and is sufficiently conductive for the purpose. In combination with iron, the potential difference is about 1 V, and in combination with aluminum it is about 2 V.

### *Adhesion of Electrodeposited Material*

In the experiments with columns, very small droplets enter the column and large droplets, easily settled out by gravity, come out. The columns operate continuously in this fashion for long periods of time with no sign that the electrode surfaces become inactivated, though one might have expected this to occur as coalesced material coats the electrode surfaces.

**Table I. Coalescence of Barometric Condenser Water**

| Column packing | Effluent oil content, p.p.m. |
|---|---|
| Al-Fe | 58 |
| C-Al | 0 |
| C-Fe | 0 |
| C-Mg | 1020 |

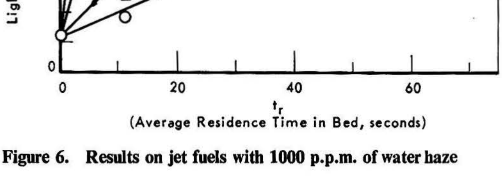

**Figure 6. Results on jet fuels with 1000 p.p.m. of water haze**

Perhaps the electrodes are not actually physically in contact with the electrodeposited particles, as has been claimed by Koelmans and Overbeek (1954), who studied the electrodepositions of solids from nonaqueous suspensions (*loc. cit.*). Their conclusions were that the particles are first brought in close proximity to the electrode by the electric field, but do not adhere to it until many seconds later, when electrolysis additionally generates a high enough local ionic concentration to flocculate the particles. In a column with flow rates fast enough to avoid the concentration of ions at electrodes but slow enough to bring the suspended particles together, electrodes may operate without contaminated surfaces.

*Consumption of Metals*

In a coalescing bed such as iron and carbon, discharge of negatively charged droplets on the iron electrode involves donating cations (such as $Fe^{2+}$) to the anions of the charged droplets, and flow of the electrons to the carbon surface, where anions (such as hydroxyl ions) neutralized the incoming cations. These reactions deplete the metal, but at a predictable rate. For example, if an emulsion in water of 200 p.p.m. of oil has droplets two $\mu$ in diameter with one charge per 100 $A^2$ (or $10^{14}$ per $cm.^2$, as is often observed), complete discharge of all droplets would consume the iron after passage of 300,000 bed volumes. If the residence time were only 3 sec., the iron should be consumed in 10 days. If larger beds were used and average residence time raised to 30 sec., the iron would last 3 months between changes.

In water-in-oil emulsions, the life of the bed should be much longer, for the surface charge density on water droplets is much lower, about $10^{11}$ per $cm.^2$, and the life of the iron for 100 p.p.m. of 2-$\mu$ droplets or 10 p.p.m. of 0.2-$\mu$ droplets would be 300,000,000 bed-volumes. At an average residence time of 3 sec., the iron would then last 30 years.

In these calculations, it is assumed that the discharge of droplets is the only reaction consuming the reactive metal. Corrosive media may also deplete some metals, especially iron. In these systems aluminum or other less corrodible metals may be especially attractive.

*Electric Potential of Charged Droplets*

The rate of electrodeposition or coalescence is proportional to the zeta-potential of the charged droplets, as indicated under **Basic Principle.** This point has been established in studies of electrodeposition of phosphorescent pigments in radio and TV tubes (Koelmans and Overbeek, 1954). Conditions leading to high zeta-potentials may favor rapid coalescence. For example, emulsions of oil-in-water may be more readily coalesced at the higher pH values leading to greater dissociation of the stabilizing acid soaps.

Zeta-potentials are also very dependent on the concentration of ionic material in the emulsion, as illustrated in Figure 7 with data of van der Minne and Hermanie (1953). These are for benzene solutions with tetraisoamylammonium picrate as the ion carrier. The electrophoretic velocity has a maximum at $10^{-5}$ mol. per liter; at lower concentrations the charge density on the carbon surface decreases and at higher concentrations, although the charge density is constant, the potential decreases because the counterions of the electric double layer are closer to the surface (Debye and Hückel, 1923). This effect may be explained by considering the electric double layer to be like a condenser with one plate representing the charged surface of a droplet and the other plate (with equal and opposite charge) representing the average location of the counterions. In such a model the distance between plates is proportional to the "thickness" ($1/\kappa$) of the double layer as given by the Debye-Hückel equation; which for 1:1 electrolytes is:

$$1/\kappa = \sqrt{\frac{Kkt}{4\pi e^2 n}}$$

where $K$ is the dielectric constant, $k$ is the Boltzman constant, $e$ the charge of the electron ($4.80 \times 10^{-10}$ statcoulombs), and

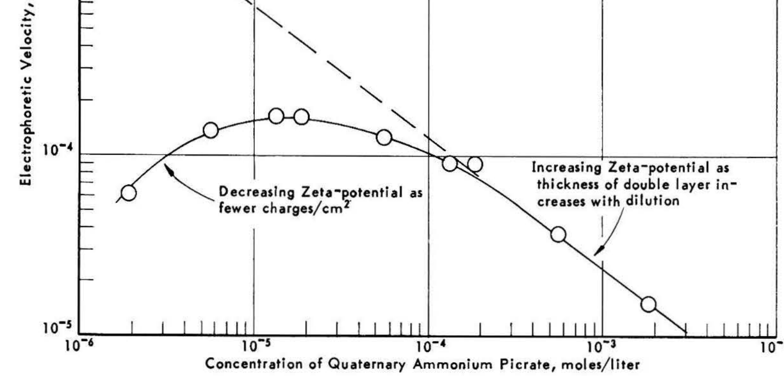

**Figure 7. Concentration dependence of electrophoretic velocity**

**Data of van der Minne for carbon black in benzene solutions of tetraisoamylammonium picrate**

$N$ the number of ions per cm.$^3$ The number of ions per cm.$^3$ should be approximately proportional to concentration of the dispersant, so one might expect $1/\kappa$ to be inversely proportional to the square root of concentration, and therefore the zeta-potential should increase upon dilution inversely with the square root of concentration. Figure 3 shows a somewhat steeper increase with dilution (the 0.7 power instead of the 0.5 power), but illustrates the general expectation that dilution increases zeta-potential.

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# Decarbonation and Deaeration of Water By Use of Selective Hollow Fibers

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■ Certain volatile contaminants may be removed from water and waste water at atmospheric pressure through a process of selective separation using small bore, hollow fiber membranes. Selective hollow fiber separation of carbonate from water has been investigated as an alternative to air blowing during water treatment. Complete carbonate removal as high as several hundred p.p.m. $CaCO_3$ was easily obtained with the laboratory selective separator. Dissolved oxygen was reduced at least 96% from initial saturation values using the same system. The permeability coefficients calculated from the experimental data were used to make an estimate of the separator size required for a given flow rate and $CO_2$ removal. Ammonia and low molecular weight organics removal is an additional area of application proposed for the waste water field.

Selective separation using a liquid and a gaseous phase is an entirely new concept of membrane application in the water and waste water treatment field. The process has been considered for separation of organic solvents in industrial processes for several years (Choo and Sanders, 1961; Michaels, Bixler, *et al.*, 1967), but has not been economically competitive because of the large concentrations of the components to be separated. However, the relatively low concentrations of pollutants in water and waste water indicate potential use for the process in this field.

It is proposed that this unit operation can supplement the more common membrane processes as reverse osmosis or electrodialysis. The large specific surface areas and selectivity achieved with these membranes allow removal of specific contaminants not possible with electrodialysis or reverse osmosis. This unit operation removes volatile inorganic or organic solutes from the water stream leaving "pure" water while reverse osmosis removes "purified" water from a stream contaminated with certain organic solutes or inorganic ions. Electrodialysis removes inorganic ions from contaminated water leaving "purified" water.

*Discussion*

The theory of separation of the pollution from water is based on the specificity of a membrane for a specific solute over that of water, *i.e.*, the pollutant is preferably transferred and the purified water remains in the main stream. The overall membrane flux for this process need be only a very small fraction of that for reverse osmosis since the solute is the transferred material. In addition, the only pressures involved are those necessary to compensate for hydraulic losses within the separator.

The common method of describing permeability of a material through a membrane is described (Li, *et al.*, 1965) as:

$$P = D \times S \tag{1}$$

where $P$ = permeability of solute through the polymer fiber wall
$D$ = diffusivity of solute in the polymer fiber wall
$S$ = solubility of solute in the polymer fiber wall

It can be seen from the equation that permeability is a direct function of the product of diffusivity and solubility. The diffusivity may ideally be expressed by Ficks equation:

$$D = F\frac{\gamma l}{\gamma C} \tag{2}$$

where $F$ = flux through membrane
$l$ = membrane thickness
$C$ = concentration inside membrane
$D$ = diffusivity of solute in the membrane

The solubility of the material in the membrane may ideally be expressed by Henry's law:

$$C_{\text{Soln}} = K \times C_{\text{membrane}} \tag{3}$$

where $C$ = concentration on either side of the membrane-water interface
$K$ = distribution constant

The permeability of a component, in other words, may be increased by either an increase in solubility in the membrane or an increase in diffusivity in the membrane.

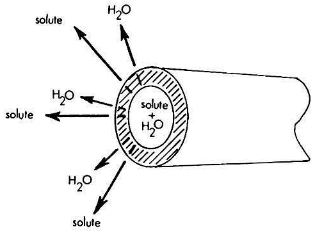

Figure 1. Schematic of hollow fiber selective separation

The separation of two components will be dependent on the relative permeabilities of the components, described as "permselectivity" (Choo and Sanders, 1961).

$$PS_{B/A} = \frac{P_B}{P_A} \tag{4}$$

where $PS_{B/A}$ = permselectivity of $B$ over $A$
$P_B$ = permeability of $B$
$P_A$ = permeability of $A$

The rule of thumb—likes dissolve likes—is a good rule to follow in choosing a suitable fiber material to separate a solute from water. The solute should be more soluble than water in the polymer material.

As a solute containing water passes through the fiber, both pollutant and the water (at a much slower molar rate) permeate into a vacuum or $N_2$ sweep gas (Figure 1). The diffusion of the solute is caused by the concentration gradient across the fiber wall.

Permeability coefficients for the hollow fibers were calculated using the local instantaneous equation for Fickian diffusion derived for radial diffusion, linear variation of concentration gradient with flux, and Henry's law. The derivation is analogous to that for heat transfer (McCabe and Smith, 1956). The resulting equation is:

$$P = \frac{(X)(l)}{(t)(\bar{A}_L)(\Delta\bar{C}_L)} \tag{5}$$

where $P$ = permeability of solute
$X$ = solute transferred per unit time
$l$ = fiber wall thickness
$t$ = time
$\bar{A}_L$ = transfer area based on log mean radius
$\Delta\bar{C}_L$ = log mean concentration driving force
= $\bar{C}_L$ liquid; since assume C gas is zero

*Carbonate Removal from Water*

Initial tests were undertaken for removal of inorganic gaseous pollutants from water because they follow ideal relationships more closely than volatile organics.

Carbonate removal and deaeration were investigated as a potential application of the selective hollow fiber separation process. If carbonate removal is required from boiler feed, desalination feed, or process water it is usually accomplished by air blowing at reduced pH where the carbonate exists nearly all as $CO_2$. However, this treatment requires a sizeable tower with forced air allowing microbial contamination of the water. This microbial contamination may foul the following processes. The succeeding experimentation using a hollow fiber selective separator is shown to be feasible as an alternate for the air blowing and vacuum deaeration.

*Experimental Procedures*

The hollow fiber separators used in this investigation contained approximately 5000 hollow fibers, 45 $\mu$ o.d. and 25 $\mu$ i.d. The separators were constructed in a fashion similar to a shell and tube heat exchanger (Figure 2). The untreated water for the research experiments was fed through the bores of the hollow fibers and the $CO_2$ removed from the shell by vacuum. The $CO_3^{-2}$ free water emerges from the opposite end of the separator.

Bore feed is not practical for full-scale operation because of pressure drop and particulate plugging. However, it was used in the research so that the exact effective surface area would be known for calculation of permeability coefficients. Actual operation on a large scale would utilize shell-side feed.

The experimental feed solutions were prepared by addition of $Na_2CO_3$ to distilled water and adjustment of the pH with HCl. The removal of $CO_2$ was quite easy so concentrations as high as 500–700 p.p.m. $CaCO_3$ were needed so that a residual would exist in the effluent.

The carbon dioxide levels in feed and effluent were determined from Beckman Total Carbon Analyzer results.

*Experimental Results and Discussion*

Several hollow fiber materials were compared initially to determine feasibility of the $CO_2$ separation from water and to find the best candidate for further investigation. The $CO_2$ removals were found to be the following: Dacron 44%; nylon 46%; polyethylene 81%; and polypropylene 99%. It is readily apparent that the less polar materials, polypropylene and polyethylene, yielded twice the $CO_2$ removals of the more polar materials nylon and Dacron. Succeeding tests using polypropylene and polyethylene at a pH less than 4.3 showed the two fibers to be approximately equivalent in $CO_2$ permeability.

A polypropylene hollow fiber selective separator was used for further testing because of its availability combined with its good $CO_2$ permeability. In order to simplify calculations of the permeability coefficients, the pH was adjusted to less than 4.3 to convert the carbonate to $CO_2$.

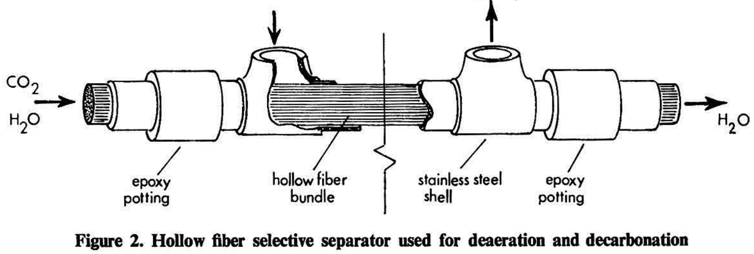

Figure 2. Hollow fiber selective separator used for deaeration and decarbonation

The permeability coefficient for $CO_2$ was found to vary considerably over the normal range of temperature of raw waters. For example, at a temperature of 5.9° C. the permeability coefficient was only 371 $\mu$mol. $CO_2$-$\mu$/hr. molar cm.$^2$ while that for 30° C. was 2141.

It was further found that Arrhenius' relationship was followed as shown in Figure 3 where log of permeability coefficient is plotted *vs.* the reciprocal of absolute temperature and a straight line results. This may be taken as evidence that the permeability of $CO_2$ through polypropylene was diffusion limited and that $CO_2$ interaction with the polymer was small (Tuwiner, 1962). Henry's law was probably followed.

The activation energy of permeation, $E_p$, was determined from the linear form of the Arrhenius relationship:

$$\log P = \log P_0 - E_p/R(1/T) \tag{6}$$

where $P$ = permeability of $CO_2$ at temperature, $T$
$P_0$ = permeability of $CO_2$ at infinite temperature
$-E_p/R$ = slope of plot, Figure 3
$E_p$ = activation energy of permeation
$R$ = gas law constant
$T$ = absolute temperature, °K.

This value of $E_p$ was found to be 11.9 Kcal./mol. which is 2.8 Kcal. higher than the result reported for a system of dry $CO_2$ and polypropylene (Myers, *et al.*, 1959). This increase is interpreted (Vieth, 1969) as the effect of limited swelling of the polypropylene by water to a greater degree at higher temperatures than at lower temperatures.

Since the data followed the Arrhenius relationship, permeability was assumed to be a constant and an equation was developed to calculate the theoretical size of separators.

$$R = \frac{(P)(\bar{C}_L)(\bar{A}_L)}{(C)(l)} \tag{7}$$

where $R$ = flow rate of water through the permeator
$P$ = permeability of $CO_2$
$\bar{C}_L$ = log mean concentration of $CO_2$ in the water
$\bar{A}_L$ = log mean transfer area
$C$ = change in concentration of $CO_2$ in the water stream
$l$ = fiber wall thickness

If the permeability coefficient of $CO_2$ is taken as 1050 $\mu$mol. $CaCO_3$-$\mu$/hr. molar cm.$^2$ at 20° C. the required size of a separator to remove 99% of 250 p.p.m. alkalinity as $CaCO_3$ for a flow of 10,000 g.p.d. would be only 7.7 ft.$^3$ This is based on a specific surface area of 9000 ft.$^2$/ft.$^3$ for the separator.

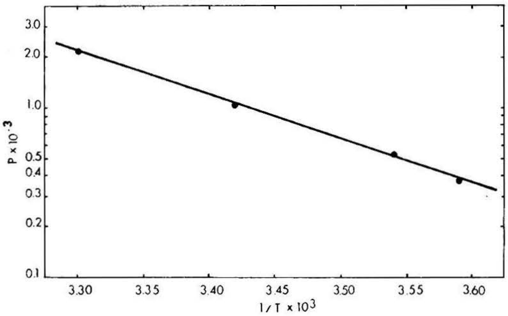

**Figure 3. Arrhenius relationship of $CO_2$ permeability through polypropylene hollow fibers**

**Table I. Dissolved Oxygen Removal Using Selective Hollow Fiber Separators**

| | Level of d.o. | | |
|---|---|---|---|
| Temp. (°C.) | Feed (p.p.m.) | Effluent (p.p.m.) | % Removal |
| 8 | 7.6 | 0.2 | 97 |
| 30 | 7.5 | 0.3 | 96 |

Checks using the Winkler analysis for dissolved oxygen on the feed and effluent indicated that in addition to $CO_2$ removal it is possible at the same time to remove the dissolved oxygen from water. The d.o. level was reduced from saturation to less than 0.3 p.p.m. in the several short experiments shown in Table I. The actual d.o. level may have been lower than shown since the Winkler analysis is not accurate in the very low ranges without modification. Removal of d.o. was probably even greater than the 96% observed.

The authors believe that $N_2$ gas will be similarly removed so that the water will be deaerated and decarbonated in the same operation.

A comprehensive study of the economics of various decarbonation and deaeration systems for desalination concluded that use of a decarbonator is uneconomical alone but may be useful in conjunction with a deaeration system (Hammond, *et al.*, 1967). Selective separation appears to fit this dual application.

It has also been proposed that selective separation of $CO_2$ might be used in conjunction with ion exchange for boiler feed or process waters where $H^+$ exchange precedes selective carbonate separation and $OH^-$ exchange follows. External pH adjustment would not be necessary using this sequence.

### *Summary and Conclusion*

The use of selective hollow fibers for removal of certain pollutants from water is a new application of membranes to waste water treatment. Removal of carbonate from water using a polypropylene hollow fiber separator has been demonstrated as feasible. A separator of only 7.7 ft.$^3$ volume would theoretically be required to remove 99% of the alkalinity in a feed of 10,000 g.p.d. and 250 p.p.m. initial $CaCO_3$ alkalinity. The same hollow fiber separator will remove at least 96% of the d.o. at the same time carbonate is being removed. However, pilot-scale tests should be carried out before accurate economic estimates of the process are made.

There also appear to be numerous areas in waste water treatment where such a principle as selective hollow fiber separation may be needed. Ammonia removal from waste water at high pH is currently being investigated by the authors.

In addition, another very promising area is treatment of industrial wastes containing volatile organic solvents, for instance low molecular weight hydrocarbons. These solutes could be removed from the process waste stream with a hollow fiber material tailored specifically to that pollutant. There may also be economic value in recovery of the material.

### *Acknowledgment*

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# Adsorption and Desorption of Inorganic Phosphorus by Lake Sediments in a 0.1*M* NaCl System

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■ Noncalcareous lake sediments generally adsorbed and retained more added inorganic P than calcareous lake sediments. Sediments which retained the most added P during adsorption tended to release the least P during a subsequent desorption at all levels of added P. The net amount of added P adsorbed (following adsorption and desorption) was lowest for calcareous sediments, with one exception, at the highest level of added P (50 μg. of P per ml.). The reactions involved in the adsorption and desorption of added P were not always completely reversible during the time period used in the experiment. A close relationship was found between the order of the capacity of a sediment to retain added P in the laboratory and the levels of native total P and inorganic P in the sediment.

The capacity of lake sediments to retain or release P is undoubtedly one of the important factors which influence the concentration of inorganic and organic P in lake waters. Although several reports have discussed the predicted effects of various physical and chemical parameters on the behavior of sediment P (Golterman, 1967; Olsen, 1966) few investigations have involved evaluation under controlled conditions of the amounts of P adsorbed and desorbed by sediments.

This paper is concerned with an investigation of the adsorption and desorption of inorganic P in a 0.1*M* NaCl system by lake sediments of contrasting chemical composition. Results are discussed in relation to the amounts of native total P and inorganic P in the sediments.

## *Materials and Methods*

**Samples.** Sediment samples were collected in late 1968 and early 1969 from eight Wisconsin lakes: Lakes Wingra, Monona, and Mendota in southern Wisconsin; Devils Lake in south-central Wisconsin; and Crystal, Little John, Trout, and Minocqua lakes in northern Wisconsin (Table I). Characteristics of most of these lakes and general features of the sediments have been described elsewhere (Frey, 1963; Murray, 1956). Briefly, Wingra and Little John are relatively small and shallow in comparison to the others. Based on visual assessment of productivity and the extent of oxygen depletion in the hypolimnetic waters during the period of thermal stratification, Lakes Wingra, Monona, Mendota, and Little John are considered eutrophic, Trout and Minocqua mesotrophic, and Devils and Crystal oligotrophic.

Samples were taken from a single site in the deep-water area of Lakes Monona, Mendota, Devils, Crystal, and Little John. For Lake Wingra, seven sites distributed over the entire lake were sampled. The seven Wingra samples obtained varied little in a wide range of chemical properties such as organic C and total P contents. Three samples (Wingra 1, 4, and 7) were chosen as representative of the original seven. The three samples taken from Trout Lake were from widely separated locations; Trout 1 was taken from the deepest area of the lake. Minocqua 1 was taken from a bay located immediately west of the town of Minocqua. In summer, this bay shows obvious signs of eutrophication, presumably due to the influence of the town. In the remainder of the lake, eutrophication is not evident. Minocqua 2 was taken from one of the deepest locations in the main portion of the lake.

Sediments were obtained with an Ekman dredge which grouped several dredge samples for the bulk sample from each site. Bulk samples were stored at 4° C. in sealed glass containers. Subsamples for chemical analyses were either freeze-dried, air-dried at 25° C., or used directly from the bulk sample in the wet state ("undried" samples).

**Analytical Methods.** Sediment pH was measured with a glass electrode on the undried sediment. Total C was determined by combustion (Piper, 1944) of freeze-dried sediment; values for organic C were obtained by subtracting $CO_3 - C$, determined according to the manometric procedure of Leo (1963), from the total C content. Total P was determined by

$Na_2CO_3$ fusion (Syers, Williams, *et al.*, 1968) by use of freeze-dried sediment ground to pass through a 100-mesh sieve. Total organic P was determined on <100-mesh material by the Mehta, Legg, *et al.* (1954) extraction procedure (Sommers, Harris, *et al.*, in press). Total inorganic P was calculated by the difference between total P and total organic P values. All results were expressed on an oven-dried (110° C.) basis.

To study the adsorption by the sediments of inorganic P added in the laboratory, a weight of each undried sediment equivalent to 0.5 g. of oven-dried material was transferred to a preweighed 100-ml. polypropylene centrifuge tube. Water was added to bring the liquid phase weight to 25 g. and 25 ml. of 0.2*M* NaCl containing 0, 5, 20, and 100 $\mu$g. of P per ml. as $KH_2PO_4$ was added. A 0.1*M* NaCl system was used to facilitate particle settling during centrifugation. The tubes were agitated on a wrist-action shaker for 12 hr. at 25° C., centrifuged, and an aliquot of the supernatant taken for the determination of inorganic P by the colorimetric procedure of Murphy and Riley (1962). The supernatant was removed and the tubes were again weighed to determine the volume of solution entrapped in the residue. Measurement of P desorption from the sediment involved addition to the residue of an appropriate volume of 0.1*M* NaCl to bring the total volume to 50 ml.; the 12-hr. extraction, recovery, and removal of the supernatant and the inorganic P colorimetric determination were carried out as above. The residue was weighed immediately after centrifugation and decantation following the desorption step and again after drying at 110° C. overnight. Calculation of the changes in the amount of P adsorbed and subsequently desorbed per g. of oven-dried sediment allowed for the amount of P in the solution entrapped in the residue following adsorption, the weight of entrapped NaCl in the residue following desorption, and the release of P into solution by samples to which no P was added.

### *Results and Discussion*

**Sediment Characteristics.** Sediment samples provided a wide range of chemical composition (Table I). The $CaCO_3$ equivalent ranged from <0.5% in Devils and the four northern lakes to 62% in Wingra 7. Values for pH ranged from 4.4 in Trout 1 to approximately 7 in the calcareous sediments from the southern lakes. Northern lake sediments contained appreciably more organic C than sediments from the other lakes. Total P varied more than tenfold and was higher in the noncalcareous sediments (Table II). Sediments from deep-water areas of Trout and Minocqua contained more total P than sediments from shallower areas of the same lake. This increase in total P content of lake sediments with an increase in depth of the water column is well established (Rohlich, 1963) and is presumably due to natural sorting processes which carry the fine textured material to the deep-water areas of the lake. Consequently, the similarity in total P values for the samples from Lake Wingra is not surprising in view of the uniformity in water depth and small size of the lake. Values for total P in the deep-water areas of Monona and Mendota were approximately twice as high as those for Wingra, although all three lakes are calcareous and occur within close proximity to each other. Total P was higher in the Devils sediment than in sediments from the calcareous southern lakes but was lower than in the sediments from noncalcareous lakes from northern Wisconsin with the exception of Trout 5.

**Adsorption-Desorption.** At each level of added inorganic P, the three calcareous Wingra sediments adsorbed the least amount of P during the adsorption step (Table II). More added P was adsorbed by the Monona and Mendota sediments, but, in general, the five calcareous sediments adsorbed less added P than the noncalcareous sediments. The Minocqua 2 sediment adsorbed 96% of the added P at the highest level of added P (5000 $\mu$g. of P per g. of oven-dried sediment): this is equivalent to 4800 $\mu$g. of P per g. of oven-dried sediment.

Sediments which adsorbed the most P during the adsorption step usually released the least P during the subsequent desorption step at all initial levels of added P. At the highest level of added P (5000 $\mu$g. of P per g.), the amount of added P released from the sediments during the desorption step, expressed as a percentage of added P adsorbed, was generally greater for calcareous sediments (13 to 41%) than for noncalcareous sediments (3 to 17%).

The net adsorption of added P, expressed as a percentage of total added P, was lower, with one exception (Trout 5), for the calcareous than for the noncalcareous sediments at the lowest and intermediate levels of added P: this was also true, with two exceptions (Trout 5 and Devils 1), at the highest level of added P. Values for net P adsorption at the lowest level of added P ranged from 28% for the calcareous Wingra 4 sediment to 99% for the noncalcareous Little John 1, Trout 1, and Minocqua 2 sediments. With an initial added P level of 5000 $\mu$g. of P per g., net adsorption was lower on a percentage

**Table I. Location and Some Chemical Characteristics of the Lake Sediments**

| Lake and sample number | | County | Trophic state[a] | Depth,[b] m. | pH | $CaCO_3$ equivalent, % | Org. C, % |
|---|---|---|---|---|---|---|---|
| Wingra | 1 | Dane | eutrophic | 3 | 7.0 | 47.3 | 6.8 |
| Wingra | 4 | Dane | eutrophic | 3 | 6.9 | 56.5 | 8.0 |
| Wingra | 7 | Dane | eutrophic | 3 | 6.9 | 62.3 | 6.8 |
| Monona | 1 | Dane | eutrophic | 13 | 7.0 | 33.1 | 7.4 |
| Mendota | 1 | Dane | eutrophic | 22 | 7.0 | 26.9 | 7.7 |
| Devils | 1 | Sauk | oligotrophic | 14 | 5.3 | <0.5 | 7.5 |
| Crystal | 1 | Vilas | oligotrophic | 16 | 5.3 | <0.5 | 25.1 |
| Little John | 1 | Vilas | eutrophic | 6 | 5.7 | <0.5 | 25.9 |
| Trout | 1 | Vilas | mesotrophic | 32 | 4.4 | <0.5 | 12.9 |
| Trout | 2 | Vilas | mesotrophic | 33 | 6.5 | <0.5 | 15.7 |
| Trout | 5 | Vilas | mesotrophic | 15 | 6.3 | <0.5 | 22.9 |
| Minocqua | 1 | Oneida | eutrophic | 9 | 6.9 | <0.5 | 13.0 |
| Minocqua | 2 | Oneida | mesotrophic | 15 | 6.7 | <0.5 | 16.0 |

[a] Based on observation and the extent of oxygen depletion in the hypolimnion during thermal stratification.
[b] Depth of water column at sampling site.

Table II. Adsorption and Desorption of Added Inorganic Phosphorus by Lake Sediments

| Lake and sample number | Added P adsorbed as % total added P | | | Added P desorbed as % added P adsorbed | | | Net added P adsorbed as % total added P[a] | | | Total native P (p.p.m.) | Total native inorganic P (p.p.m.) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | for added P level (μg. of P per g.) of | | | | | | | | | | |
| | 250 | 1000 | 5000 | 250 | 1000 | 5000 | 250 | 1000 | 5000 | | |
| Wingra 4 | 42 | 16 | 6 | 33 | 38 | 41 | 28 | 10 | 4 | 664 | 362 |
| Wingra 1 | 50 | 24 | 8 | 28 | 35 | 38 | 36 | 15 | 5 | 718 | 441 |
| Wingra 7 | 44 | 23 | 10 | 31 | 36 | 34 | 30 | 15 | 7 | 555 | 340 |
| Monona 1 | 79 | 48 | 19 | 21 | 22 | 25 | 62 | 37 | 14 | 1260 | 940 |
| Trout 5 | 92 | 57 | 20 | 5 | 14 | 17 | 87 | 49 | 16 | 986 | 420 |
| Devils 1 | 98 | 89 | 37 | 0 | 6 | 15 | 97 | 83 | 32 | 1630 | 1170 |
| Mendota 1 | 96 | 83 | 39 | 8 | 10 | 13 | 88 | 74 | 34 | 1460 | 1080 |
| Crystal 1 | 97 | 88 | 42 | 2 | 7 | 16 | 95 | 83 | 36 | 2230 | 815 |
| Minocqua 1 | 99 | 98 | 61 | 2 | 2 | 9 | 97 | 96 | 55 | 2640 | 2190 |
| Little John 1 | 100 | 99 | 67 | 0 | 2 | 6 | 99 | 97 | 63 | 4120 | 3390 |
| Trout 1 | 100 | 95 | 83 | 0 | 7 | 8 | 99 | 88 | 76 | 6090 | 5500 |
| Trout 2 | 98 | 94 | 94 | 1 | 1 | 4 | 97 | 98 | 90 | 3700 | 3140 |
| Minocqua 2 | 99 | 99 | 96 | 0 | 1 | 3 | 99 | 98 | 93 | 7000 | 6390 |

[a] Following adsorption and desorption.

basis for each sample as compared to lower levels of added P and ranged from 4% for Wingra 4 to 93% for Minocqua 2.

In Table II, the sediments have been arranged in order of increasing adsorption of added P at the highest level. This order also concurs with that of increasing net retention of added P at the same level. The most significant observation resulting from these experiments is the close relationship between the capacity of the sediment to adsorb and retain added inorganic P in the laboratory and the levels of total and inorganic native P which have accumulated in the sediments. This relationship also holds for samples taken from the same lake, as may be seen by comparing Trout 5 with Trout 1 and 2, and Minocqua 1 with Minocqua 2. For example, the Wingra samples retained the least amount of added P and contained the lowest total P whereas Minocqua 2 retained the greatest amount of added P and contained the highest amount of total P and total inorganic P. In general, the relationship between total P and added P retained was better than that between total inorganic P and P retention.

The data suggest that the P retention capacity of a sediment is an important factor determining the levels of P which accumulate in lake sediments under natural conditions. The lower capacity of the calcareous sediments to retain P under natural conditions or in the laboratory suggests that $CaCO_3$ is less effective in retaining P than the components responsible for P retention in the noncalcareous sediments.

No consistent relationship appears to exist between lake eutrophication and P retention capacity. Sediments from Wingra, one of the most eutrophic lakes, showed the lowest P retention capacity whereas the sediment from Little John, also eutrophic, showed a high retention capacity. However, the Minocqua 1 sample (eutrophic) had a much lower P retention capacity than Minocqua 2 (mesotrophic). Moreover, the P retention capacity of the Mendota sediment (eutrophic) was generally lower than that of the Trout sediments (mesotrophic). It is apparent, therefore, that the state of lake eutrophication cannot be explained solely on the basis of the capacity of sediments to retain P.

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**COMMUNICATION**

# On the Significance of Metal Complexing Agents in Secondary Sewage Effluents

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■ Preliminary experiments in this laboratory using recent advancements in anodic stripping techniques have demonstrated that two distinct molecular weight fractions of secondary sewage effluents complex metals. One fraction has a molecular weight similar to that of synthetic chelators and has proved effective in stimulating algal growth.

At present, control of eutrophication in natural waters is being attempted by reducing nutrient inputs (*i.e.*, phosphorus and nitrogen) to these waters from sewage effluents. However, there is some question whether the growth stimulation caused by secondary sewage effluents can always be totally accounted for by the nitrogen and/or phosphorus levels in these effluents (McGauhey, Rohlich, *et al.*, 1968; Stewart and Rohlich, 1967). Many compounds, both inorganic and organic, could be responsible for the effect. Vitamin $B_{12}$ has been identified by Hoover, Jasewicz, *et al.* (1951) as one of the compounds present in sewage which could be effective in stimulating algal growths. Other compounds which could be responsible include: trace metals, organic growth factors, and metal complexing agents.

The chelation or complexing of metals by organic compounds has been demonstrated by several workers to cause significant increases in algal production (Johnston, 1964; Shelske, 1962; Shapiro, 1964). While some of these experiments have been conducted utilizing synthetic chelating agents such as EDTA, the chelation of iron by naturally occurring humic substances has been demonstrated by Shapiro (1964) to be significant in increasing algal growth. Prakash and Rashid (1968) have demonstrated that humic substances of natural origin increase growth rates of marine algae.

It is reasonable to assume that organic chelating substances, if present in sewage effluents, could stimulate algae growth by making trace metals already present in the receiving water more available or reduce growth by forming stable unavailable complexes. We have attempted, as described below, to find such substances.

## *Methods*

Secondary sewage effluent was collected from the Ann Arbor activated sludge plant prior to chlorination. The samples were filtered through 0.45-$\mu$ membrane filters to remove bacteria and other solids. Spikes of copper containing 700 ng. were added to 10-ml. aliquots of the filtrate. Molecular weight fractionations were then made on the 10-ml. samples using 2.5 × 45 cm. columns of Sephadex G-50 medium. To prevent problems of coagulation and precipitation within the column, the columns were eluted at a flow rate of 1.3 to 1.7 ml./min. with approximately 0.02 $N$ NaCl of the same conductivity and pH as the sewage. Eluant fractions of 8 ml. were collected for copper and total carbon analysis by infrared absorption.

Copper was determined as free or bound using the composite mercury graphite electrode and anodic stripping technique described by Matson, Roe, *et al.* (1965, 1967). Each 8-ml. fraction was plated at a potential of $-0.7$ V *vs.* SCE for 3 to 15 min. and then stripped at a sweep rate of 40 mV/sec., giving a value for free or labile copper ion. After this plating step, 50 $\mu$l. of perchloric acid was added to the sample to release the complexed copper, and the plating and stripping steps were repeated giving a value for acid-exchangeable copper. Digestion experiments with ammonium persulfate indicate that acid-exchangeable copper is equivalent to total copper in this type of sample.

By use of a modification of techniques reported previously by Allen, Matson, *et al.* (in press), various sewage fractions and samples of raw sewage were titrated by adding successive 100-ng. aliquots of copper to the sample at a plating potential of $-0.7$ V *vs.* SCE until a copper peak was observed.

Exchange experiments were carried out by following the technique of Matson (1968) with $Fe^{+3}$ on sewage fractions saturated with copper to determine the extent and rate of exchange.

Preliminary algal growth studies were conducted with each of the molecular weight fractions, isolated in quantity using larger 4.5-in.-diameter columns, to test their biological significance. The studies were conducted with natural algal populations enclosed in borosilicate glass containers to which the nutrient materials in question were added.

In the Third Sister Lake experiment, the containers were suspended in the lake for incubation, while in the Lake Michigan experiment, the containers were incubated on shipboard in a water bath at lake temperature. C-14 uptake was used as a measure of response to the additions.

## *Results and Discussion*

Figure 1 shows a typical example of the distribution of copper and the associated quantities of total carbon obtained from the Sephadex separations. Two rather distinct molecular weight fractions are apparent. The large molecular weight fractions at the breakthrough volume of the column (∽10,000 mol. wt.), contained about 100 ng. of copper while the smaller molecular weight fractions (500 to 1000 mol. wt.) contained about 700 ng. No free copper was found in any fractions using the 700 ng. spike.

The concentration of ligands determined by titration in this and eight other sewage samples ranged from $8 \times 10^{-5}$ to $1 \times 10^{-6} M$ equivalent binding sites for copper. Copper made unavailable for electrochemical plating through complexa-

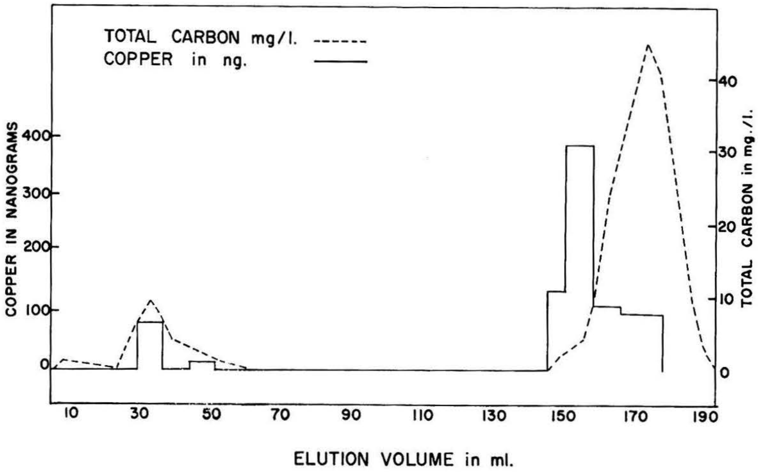

**Figure 1. Distribution of carbon and of metal binding capacity in secondary sewage fractions obtained from Sephadex separations**

**Table I. Algal C-14 Uptake in CPM (Light-Dark)**

| | Third Sister Lake<br>No. sewage ligands | | Sewage ligands (low mol. wt.) $1 \times 10^{-7}$ *M*<br>(equivalents of copper) | |
|---|---|---|---|---|
| Date | No. Fe | Fe ($5 \times 10^{-8}$ *M*) | No. Fe | Fe ($5 \times 10^{-8}$ *M*) |
| 4-25-69 | 250 | 215 | 586 | 780 |
| 4-28-69 | 256 | 209 | 598 | 717 |
| 4-30-69 | 343 | 319 | 495 | 620 |
| 5-2-69 | 293 | 312 | 532 | 406 |

| | Lake Michigan | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | Low mol. wt. ligands | | High mol. wt. ligands | |
| Date | Control no. Fe | Fe ($3 \times 10^{-7}$*M*) | Fe + EDTA ($3 \times 10^{-7}$*M*)($1 \times 10^{-7}$*M*) | No. Fe | Fe ($3 \times 10^{-7}$*M*) | No. Fe | Fe ($3 \times 10^{-7}$*M*) |
| 4-20-69 | 596 | 518 | 729 | 1107 | 1096 | 794 | 644 |
| 4-21-69 | 485 | 658 | 592 | 677 | 776 | 613 | 516 |

tions with ligands in the sewage was released by $Fe^{+3}$ as well as by acid, indicating that the ligands are also available for iron complexation.

Lead in the sewage also approximately followed the copper but was not quantitatively determined.

In one unreplicated trial (Table I) on Third Sister Lake in the Saginaw Forest, Ann Arbor, Michigan, the lower molecular weight fraction, both alone and when combined with iron, had an effect in stimulating algal growth.

A second trial (Table I) in Southern Lake Michigan water approximately 15 miles from Chicago showed a smaller but still measurable effect for low molecular weight sewage ligands. The high molecular weight fractions which bind the metals more strongly and might be less likely to pass the cell membrane, showed a very slight effect. In both trials, a marker of vitamin $B_{12}$ was employed as a control on the column used to isolate the ligand material to ensure that the effects seen would not be caused by uncomplexed $B_{12}$ in the sewage.

## *Conclusions*

Fractions isolated from secondary sewage effluent containing organic ligands for metal cations show a definite effect in increasing the growth of algae. Effort is being made at present to rule out the possibility that other substances in the sewage fractions, such as vitamins, plant hormones, or organic phosphate, could be responsible for the stimulation of algal growth detected.

## *Acknowledgment*

The authors gratefully acknowledge the assistance of the crew of the research vessel, *Inland Seas*, Great Lakes Research Division, University of Michigan.

## *Literature Cited*

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# new literature digest

**Fume scrubber.** A 4-page bulletin B-760 describes the model 760 crossflow fume scrubbers for removal of mist, gases, and solid pollutants in the fertilizer, chemical, pulp and paper, steel, plating, and metal finishing industries. Heil Process Equipment Corp. **91**

**Combustible gas detector.** Brochure describes the new models 170 and 175 detectors for hydrogen, hydrocarbon gases, alcohols, ketones, ethers, and the like. The detector can be used for pipelines, refineries, process industries, and aerospace applications for fixed installations. General Monitors, Inc. **92**

**Solvents for pollution studies.** A 4-page catalog describes 47 solvents which can be used to extract residues from air pollution or water pollution samples, pesticides residues in foods, and other spectrophotometric uses. Burdick & Jackson Laboratories, Inc. **93**

**Waste water analysis.** Bulletin 69-12A describes an automated titration procedure for low-level COD analyses. The automated procedure follows APHA Standard Methods except that end points are measured potentiometrically rather than colorimetrically. Fisher Scientific Co. **94**

**Slurry feed control.** A 2-page leaflet describes the operation of Mixmeter in a step-by-step sequence to show how the three major variables of influent volume, influent quality, and concentration of slurry are automatically compensated for in the Mixmeter, a system which treats millions of gallons of water per day. Shirley Machine Co. **95**

**Temperature control guide book.** An 8-page guide illustrates the complete line of 400 series indicating temperature controllers. The 400 series provides precision control (±0.25% potentiometric accuracy). Thermo Electric. **96**

**Conversion booklet.** A 16-page handy reference is available for weights and measurements and their conversion factors for converting from one unit to another. Matheson Coleman & Bell **97**

**Paint Arrestors.** Bulletin PA-1507 describes Paint Arrestors, disposable air filters which trap paint and other overspray solids from the air before they reach the spray booth exhaust stack. Bulletin PA-1633 offers information for maximum efficiency of paint spray equipment with minimum air pollution. Research Products Corp. **98**

**Sewage treatment.** A 4-page brochure describes sewage treatment by a batching method. Bio-Pure manufactures secondary sewage treatment equipment in plant size ranging from 600-32,000 gallons per day. Bio-Pure **99**

**Industrial waste treatment.** Three bulletins describe continuous treatment of industrial wastes. Bulletin P-100 describes neutralization of general effluents; Bulletin P-200 describes continuous treatment of chromium wastes, and Bulletin P-300 describes treatment of cyanide wastes. Baker Bros. **100**

**Automatic GC sampler.** Data sheet 7670A describes the automatic sampler for gas chromatography which automates sample and injection. The sampler can be left unattended over weekends and is capable of 36 consecutive samples. Hewlett-Packard **101**

**Mobile facilities catalog.** A 32-page catalog describes mobile units of the truck or trailer type for technical services, instrumentation, and laboratory uses. The units are designed for use in engineering and pollution monitoring. Calumet Coach Co. **102**

**Reverse osmosis.** An 8-page brochure describes the industrial applications of ROGA water treatment systems. The systems are used for high purity water, waste treatment, potable water, water recovery, and water concentration. Gulf General Atomic **103**

**Chromatographic analyzer.** A 4-page bulletin describes the technique of gas phase controlled thermolytic dissociation (CTD) for positive identification of gas chromatographic effluents. The Pyrochrom analyzer is used in studies of odor control, pollution control, pesticide analyzers, and the like. Chemical Data Systems, Inc. **104**

**Petrochemical waste waters.** "Characteristics and Pollution Problem Associated with Petrochemical Wastes" presents a comprehensive report covering water pollution control for the petrochemical industry. Robert S. Kerr Water Research Center, Federal Water Pollution Control Administration, U.S. Dept. of Interior, P.O. Box 1198, Ada, Okla. 74820 (Write direct)

**Heated water.** Two reports describe the effects of heated water on aquatic life. The first report, "Surface Heat Exchange at Power Plant Cooling Lakes," contains findings related to temperature predictions near thermal discharge. The second report, "Effects of Elevated Temperatures Upon Aquatic Invertebrates," is a review of literature concerning effects of elevated temperatures on both freshwater and marine invertebrates. It is written for the nonprofessional biologist. Edison Electric Institute, Attn: Research Division, 750 Third Ave., N.Y., N.Y. 10017 (Write direct)

## Film

**Education on pollution.** "Pollution: Crisis in Our Environment," is a 40-minute program for audiences such as conservation and garden clubs, business, civic, church, and youth groups. Covering air, water, and land pollution, the film strip is available for $29. George H. Clement, Ward's Natural Science Establishment, Inc., P.O. Box 1712, Rochester, N.Y. 14603 (Write direct)

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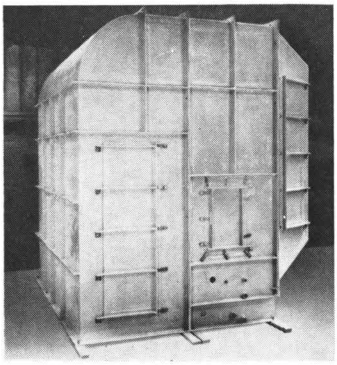
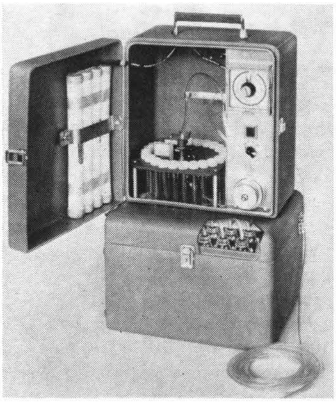
# new products digest



**Scrubber**

A new cross-flow fume scrubber has been developed to remove mists, gases, and solid pollutants generated in the fertilizer, chemical, pulp and paper, and metal industries. The compact unit uses cocurrent as well as cross-flow washing and can be fabricated of coated, lined, or stainless steel or reinforced polyester. All internal components are plastic for corrosion resistance. Heil Process Equipment Co. **61**



**Field sampler**

An automatic fluid sampler that stores each sample in a separate bottle is weatherproof, light, and battery operated for plant or field operation. Positive displacement tubing pump can draw samples up to 18 ft., and its pulsing action prevents clogging. Automatic reversing purges sample line to cut cross contamination. Sigmamotor, Inc. **62**

**Air sampler**

A long-term air sampling kit has a $^1/_6$ h.p. split phase induction motor protected against overheating, making it suitable for lab or field studies. Flow rate is adjustable to 68 liters/min.; particles deposit on membrane or glass fiber filters, and the unit can be adapted for gases and vapors. Gelman Instrument Co. **63**

**Colorimetry**

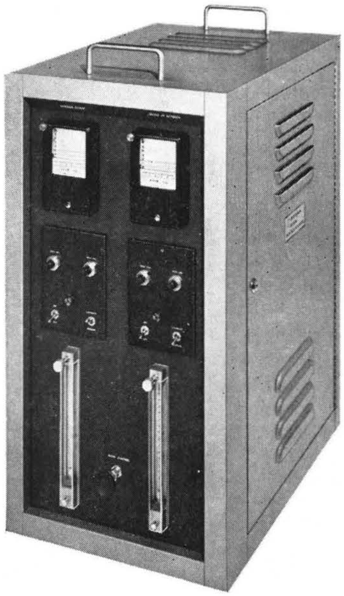
A series of automated colorimetric analyzers is designed for industrial effluents, waste water treatment, boiler feeds, and stream surveys. Picks up total cyanide, iron, silica, hydrazine, chromates, phosphates, ammonia, chlorine, TOC, and TC. Automated Environmental Systems, Inc. **64**

**Dial-a-smog**

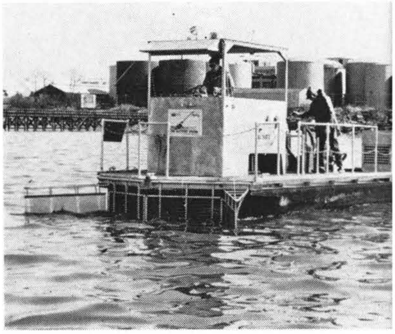
Telephone interrogation of remote pollution monitors is possible with the Data Gain DG-1000 series data acquisition equipment. A unit installed at the Orange County (Calif.), Air Pollution Control District allows the user to simply dial the remote station, and DG-1000 answers the phone and reports readings over standard telephone lines. The system can be adapted to water monitors, and remote units can be moved as often as desired. Applied Peripheral Systems, Inc. **65**

**Toxic gas analysis**

Parts-per-million levels of pollutants and toxic gases can be monitored by a new detection system. Flexible modular design permits ready incorporation of



pyrolysis trains and sequential sampling programmers, with choice of indicating, recording, alarm, or control modules. Can be calibrated for halogenated hydrocarbons, hydrogen cyanide, sulfur dioxide, sulfur hexafluoride, and most other toxic gases. Devco Engineering. **66**



**Catamaran**

An all-aluminum, 30-ft. catamaran called Mop-Cat can pick up spilled oil by means of a rotating drum at the rate of 50 barrels/hr. Recovered oil, 95% free of water, can be pumped into barges or onshore for disposal. Propelled by underwater jets, the vessel has a top speed of over 10 knots and is very maneuverable. Mop-Cat made its debut last fall, assisting in a 200,000 gallon cleanup in New York Harbor. Worthington Corp. **67**

**Hydrocarbon analysis**

The Freiz hydrocarbon analyzer uses the flame ionization principle to continuously detect and measure hydrocarbons in ambient air or internal combustion engine exhausts. The ambient air analyzer has a 7-position range switch, from 0–1 p.p.m. to 0–1000 p.p.m., and the 90% full scale response time is about 8 sec.; for auto exhaust analysis, the range covers 0–1000 p.p.m. to 0–100,000 p.p.m. and its response time is 1.5 sec. Both models have a 0–1 mV recorder and 0–10 mV output. Bendix Corp. **68**

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# bookshelf

**Biology and the Future of Man.** Edited by Philip Handler. xxiv + 936 pages. Oxford University Press, 200 Madison Ave., New York, N.Y. 10016. 1970. $12.50, hard cover.

The book is a survey of the current status of all the life sciences and brings together the reports of 21 scientific panels. It begins with origin of life and ends with the role of biology in the future of human society. The National Academy of Sciences sponsored the project on which the book is based. ■

**Ecotactics: The Sierra Club Handbook for Environmental Activists.** Edited by John G. Mitchell with Constance L. Stallings. 288 pages. Pocket Books, division of Simon & Schuster, Inc., 630 5th Ave., New York, N.Y. 10020. 1970. 95 cents, paperback.

This is a basic handbook for concerned citizens (and especially students) and was published to coincide with the April 22 nationwide teach-in. It is by no means as revolutionary as the title might indicate and contains much useful information for those not very familiar with what individual citizens can do. ■

**The Ecosystem Concept in Natural Resource Management.** Edited by George M. Van Dyne. 383 pages. Academic Press, 111 5th Ave., New York, N.Y. 10003. 1969. $16.50, hard cover. ■

**Proceedings—Fibrous Dust Seminar (November 22, 1968).** 77 pages. Industrial Hygiene Foundation, 5231 Centre Ave., Pittsburgh, Pa. 15232. 1970. $3.00, IHF members, $5.00; nonmembers, paperback. ■

**Proceedings of the Second Annual Northeastern Regional Antipollution Conference.** vi + 146 pages. University of Rhode Island, Bliss Hall, Kingston, R.I. 02881. 1969. $10.00, paperback. ■

**Congress and the Environment.** Edited by Richard A. Cooley and Geoffrey Wandesforde-Smith. xix + 277 pages. University of Washington Press, Seattle, Wash. 1970. $8.95, hard cover.

A series of essays by various authors describing the role of Congress in establishing the quality of the environment. Based on case studies, the book "points repeatedly to serious weaknesses in the capacity of government," according to the editors. ■

**Problems in Community Wastes Management.** By H. M. Ellis, W. E. Gilbertson, O. Jaag, D. A. Okun, H. I. Chuval, and J. Sumner. 89 pages. World Health Organization, 1211 Geneva 27, Switzerland. 1969. $2.00, paperback.

This WHO publication deals with solid and liquid waste management from the public health standpoint. Research needs and the controlled reuse of waste water are among the subjects covered. ■

**Approaching the Benign Environment.** Edited by Taylor Littleton. xi + 121 pages. University of Alabama Press, University, Ala. 35486. 1970. $6.00, hard cover.

The book contains three lectures from The Franklin Lectures in the Sciences and Humanities: R. Buckminster Fuller on "Education for Comprehensivity;" Eric A. Walker on "Engineers and the Nation's Future;" and James R. Killian, Jr., on "Toward a Working Partnership of the Sciences and Humanities." The Fuller lecture fills over half the pages. ■

**Air Pollution and Its Control.** By Wayne T. Sproull. 106 pages. Exposition Press, Inc., 50 Jericho Tpk., Jericho, N.Y. 11753. 1970. $4.00, hard cover.

A fairly elementary exposition of the subject, aimed at the intelligent layman. ■

**June 4 and 5**
**Vanderbilt University, Tennessee Department of Public Health, and Tennessee Stream Control Division**

9th Annual Environmental and Water Resources Engineering Conference

Sheraton Motor Inn, Nashville

Emphasis at the 2-day conference will be on the interrelationship among water resources engineering, water quality control, water supply, and municipal and industrial waste treatment. A concurrent session on air pollution control activities is scheduled.

**June 7-10**
**Technical Association of the Pulp and Paper Industry**

7th Water and Air Conference

Pick Nicollet Hotel, Minneapolis

Papers presented at the conference will cover such topics as air pollution, sludge disposal, water treatment and reuse, and effluent treatment. For information: H. O. Teeple, TAPPI, 360 Lexington Ave., New York, N.Y. 10017

**June 9 and 10**
**American Society for Metals**

Surveying Industry's Tools for Pollution Control

Cleveland, Ohio

The conference is designed for managers and technical people in the metal producing and metal working industries. It will cover the management of pollution control programs, technology to control pollution, and methods of detecting pollution. Many large steel companies will be represented. Full details: American Society for Metals, Metals Park, Ohio 44073

**June 14-19**
**Air Pollution Control Association**

63rd Annual Meeting

Chase-Park Plaza Hotel, St. Louis

Aiming to disseminate information about all areas of air pollution control, this year's meeting will include special sessions on implementation plans and national emission standards. Representatives of governmental agencies, industry, and the public sector will participate in the meeting.

**June 22-24**
**Cooling Tower Institute**

Semiannual meeting

Stonebridge Lodge, Aspen, Colo.

The program will include technical papers on the operating characteristics of cooling towers, their design and specification, and a seminar for open discussion of specific topics. Attendance of about 150 is expected. More information: Cooling Tower Institute, 3003 Yale St., Houston, Tex. 77018

**July 7 and 8**
**Federal Water Pollution Control Administration, and Georgia Institute of Technology**

Symposium on Direct Tracer Measurements of Reaeration Capacity of Streams and Estuaries

Georgia Institute of Technology

Symposium will cover theory of reaeration and laboratory and field measurement techniques. Field demonstration on a river will be included. For information: Dr. E. C. Tsivoglou, School of Civil Engineering, Georgia Tech., Atlanta, Ga. 30332

**July 8-10**
**American Society of Civil Engineers, and University of Massachusetts**

National Specialty Conference on Disinfection

University of Massachusetts, Amherst

Technical sessions and papers to be presented will cover such topics as water disinfection (including sewage and industrial wastes, combined sewage overflow, sludge, and recreational waters); effect of waste water disinfection on natural streams; and air disinfection.

**July 8-10**
**University of Colorado and others**

1970 Western Resources Conference

University of Denver

Conference theme will be "Urban Demands on Natural Resources." Speakers will discuss the effect of urbanization on the use and development of natural resources under 5 topics: Air, Water, Raw Materials, Land, and Choices. For details, contact J. J. Schantz, Jr., Denver Research Institute, University Park, Denver, Colo. 80210

**July 21-23**
**Conference of State Sanitary Engineers, Water Pollution Control Federation, and others**

National Symposium on Data and Instrumentation for Water Quality Management

University of Wisconsin, Madison

The contribution that collection and use of data can make to bettering the environment is the central theme of the conference. Papers will cover such topics as basic data requirements to evaluate water pollution and quality control programs; and a systems approach to water quality data management. Six concurrent panels will discuss pertinent subjects, including effective use of approach to water quality planning and data, operation, evaluation, and interpretation of water quality data, and remote collection, sampling, measurement, and handling of water quality data.

**July 21-23**
**University of Rhode Island, and R.I. State Technical Services**

3rd Annual Northeastern Regional Antipollution Conference

University of Rhode Island

Theme of conference is reclamation and reuse of polluted waters, air, and solid wastes. Invited speakers will explore new processing methods that will simultaneously return investment and get rid of wastes. For information: Dr. Calvin Poon, Sanitary Engineering Dept., Univ. of R.I., Kingston 02881

**July 22-24**
**Institute of Water Resources, University of Alaska**

International Symposium on Water Pollution Control in Cold Climates

University of Alaska

The 3-day symposium will be devoted to papers on waste treatment and receiving stream studies in cold climates. For information: R. Sage Murphy, Institute of Water Resources, University of Alaska, College, Alaska 99701

**July 26-August 1**
**International Association on Water Pollution Research**

5th International Water Pollution Research Conference

San Francisco

Technical sessions at this year's conference will include workshop/seminars and presentation of papers and discussion. In addition, air tours of California water projects will be available, as well as a film festival, and the international exhibits. The conference will reconvene in Hawaii from August 3-5.

**August 19 and 20**
**Water Quality Research Council**

Symposium on Water Pollution and Health

Sheraton Park Hotel, Washington, D.C.

All aspects of water supplies and contamination from the health standpoint will be covered. The conference is open to the public at large. More information: David X. Manners Co., 237 E. Rocks Rd., Norwalk, Conn. 06851

**August 24-28**
**Engineering Foundation and others**

Application of Environmental R&D to Landfill Disposal for Solid Wastes

Deerfield Academy, Deerfield, Mass.

The conference will deal with landfill disposal of solid wastes, degradation of wastes in the landfill, improving efficiency of operations, site selection, ultimate use, and guidelines for sanitary landfills. Professor E. A. Glysson of the U. of Michigan will be conference chairman. Full details from: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017.

# meeting guide

**August 24-26**
**Oak Ridge Associated Universities**
Conference on Energy and the Environment
Oak Ridge, Tenn.

Conference will deal with the implications for the urban environment and natural resources of various alternative approaches to meeting the nation's future energy requirements. For information: W. W. Grigorieff, Special Projects Office, ORAU, P.O. Box 117, Oak Ridge, Tenn. 37830

**October 28**
**New York State Action for Clean Air Committee**
Symposium on Air Pollution and Respiratory Disease
Albany Medical College, Albany, N.Y.

Symposium will be cosponsored by several local tuberculosis and respiratory disease associations and will be chaired by Frank M. Woolsey, M.D., of Albany Medical College. Emphasis will be on conditions in New York State. For details: New York State Action for Clean Air Committee, 105 E. 22nd St., New York, N.Y. 10010

**November 6-10**
**American Institute of Biological Sciences, and Federation of American Societies for Experimental Biology**
First National Biological Congress
Detroit, Mich.

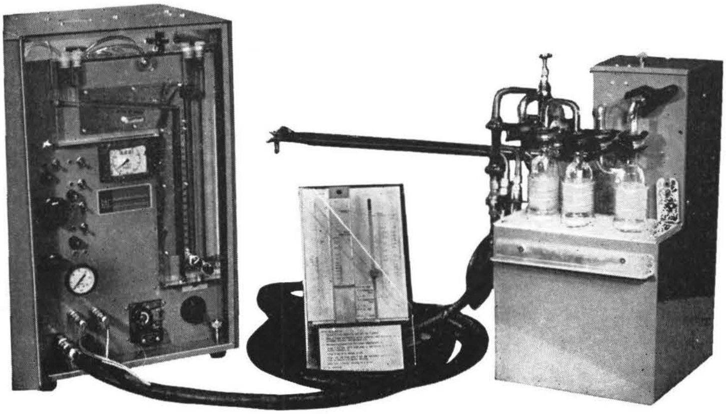
Theme of the congress will be "Man and Environment." Morning sessions will deal with scientific topics, but will appeal to both professional and layman. Evening symposia on the subject of man, environment, and public policy will bring together environmentalists and lawmakers. For full details: National Biological Congress, 3900 Wisconsin Ave., Washington D.C. 20016

## Courses

**June 15-26**
**Colorado State University**
**Institute on Urban Water Systems**
Colorado State University, Fort Collins, Colo.

Lectures, discussions, and workshop sessions are designed to familiarize urban water resource specialists with the concepts of systems analysis and optimization techniques, especially as applied to urban water resources. For details: Urban Water Systems Institute, Engineering Research Center, Foothills Campus, Colorado State University, Fort Collins, Colo. 80521

*(Continued on page 528)*



*(Meeting Guide continued)*

**June 22–August 28**
**Center for Air Environment Studies**

Training program in Air Pollution and Control Administration

Pennsylvania State University

Funded by the U.S. Public Health Service, the 10-week course is open to any person employed by an air pollution control agency, as well as college juniors, seniors, and graduate students interested in air pollution control administration career training. Credit may be obtained for the course. For information: Director, Specialist Training Programs, Center for Air Environment Studies, 226 Chemical Engineering II, Pennsylvania State University, University Park, Pa. 16802

**June 24–26**
**American Association of Professors in Sanitary Engineering**

5th Annual AAPSE Workshop

Brown's Lake Resort, Burlington, Wis.

Workshop will be on the subject of "Consulting Sanitary Engineering Practice," and is designed to help professors structure courses in which students can learn the function of the consultant in practice. Registration is limited to 60 people. Full details from: Raymond J. Kipp, Department of Civil Engineering, Marquette University, Milwaukee, Wis. 53233

**July 6–10**
**Union College**

5-Day Short Course on Modern Methods for Industrial and Product Noise Control

Union College

Course is intended for those concerned with noise and vibration control, and will provide background in the theory, measurement, and economics of noise reduction. Participants are encouraged to discuss their own noise problems at the course. Details from: W. L. Weifenbach, Union College, Carnegie Hall, Schenectady, N.Y. 12308

**July 6–10**
**University of Denver**

Short Course on Water Pollution and Waste Water Engineering

University of Denver

One-week course will cover chemistry and biology of water pollution as well as waste water treatment and disposal. Industrial and municipal waste water problems will be emphasized. For information: Dr. R. M. Wainwright, College of Engineering, Univ. of Denver, Denver, Colo. 80210

**September 22–25**
**University of California**

Short Course on Management of Solid Waste for Optimum Environmental Control

University of California, Berkeley

Four-day course intended for those concerned with environmental problems will deal with social, cultural, economic, and technological factors governing generation of solid wastes and with practical problems involved in proper management. Registration fee is $200. For details: Continuing Education in Engineering, University Extension, University of California, 2223 Fulton St., Berkeley, Calif. 94720

# professional consulting services directory

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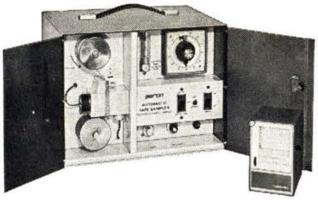

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- Interchangeable impinger tubes or diffuser tubes at minimum cost.
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- Interval time from 2 to 240 minutes.
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- Correlates with ASTM D2012.
- Gives continuous measure of $NO_2$ (or NO) in the atmosphere.
- Sensitivity 0.02 ppm or better.
- No contact of reagents or sample with pump.
- All solid state and integrated circuit components.
- Reproducibility: ±1% of full scale.
- Digital panel meter with BCD output.
- Recorder outlet.
- Sufficient reagent capacity for unattended weekend operation (72 hours).
- Adjustable to 2 ppm full scale.
- All parts easily accessible; minimum maintenance.

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- Evaluates spots at a rate of 720 spots per hour.
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