ENVIRONMENTAL Science & Technology

Emphasizing
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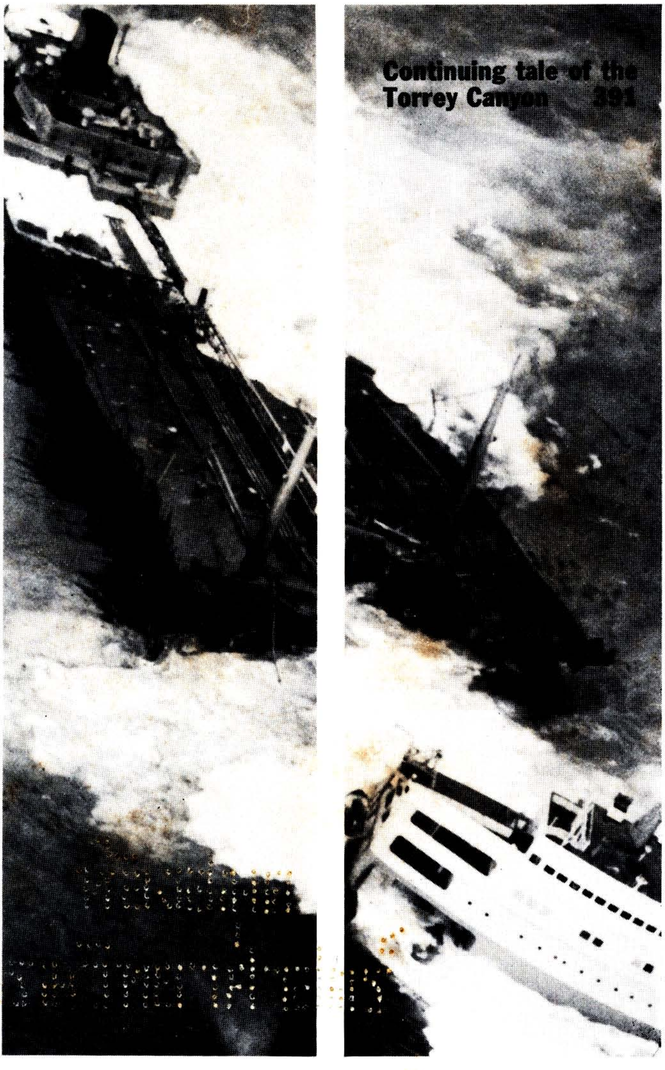
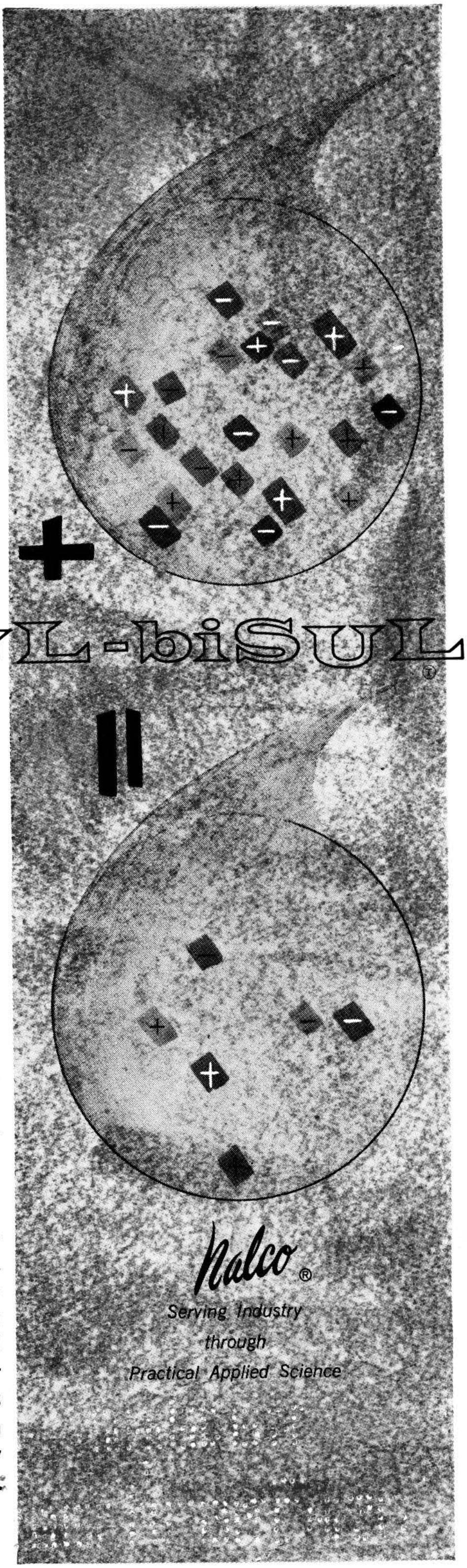
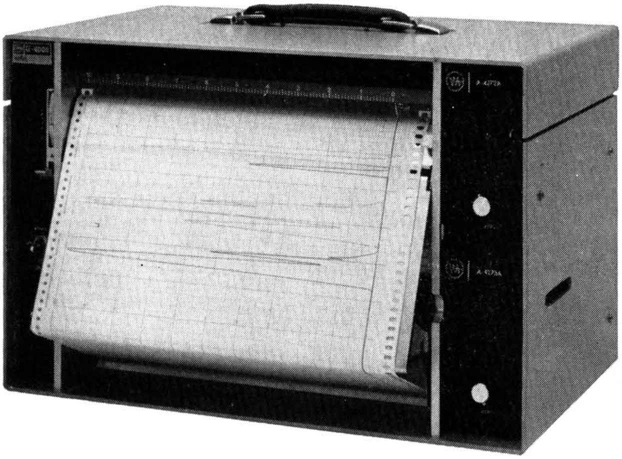
Waste
Chemistry

MAY 1967







ENVIRONMENTAL
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May 1967

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F. E. Stratton and P. L. McCarty

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J. I. Teasley

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T. Joyner, M. L. Healy, D. Chakravarti, and T. Koyanagi

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C. R. Frink

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R. S. Safferman, A. A. Rosen, C. I. Mashni, and M. E. Morris

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T. C. Purcell and I. R. Cohen

Peroxidic compounds occur in polluted air and contribute, at least in part, some of the deleterious effects on plants and animals. When ferrous thiocyanate, neutral potassium iodide, and molybdate-catalyzed potassium iodide reagents are used for the analysis of microgram quantities of a variety of peroxidic compounds by the method of kinetic colorimetry the following occur: ozone and peracetic acid give an immediate maximum color development with all three reagents; hydrogen peroxide gives slow color development with neutral KI only; and acetyl peroxide, nitrogen dioxide, alkyl hydroperoxides and peroxyacylnitrates give slow color development with all three reagents. The half-lives of these colorimetric reactions serve to identify specific oxidants.

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M. M. Rochkind

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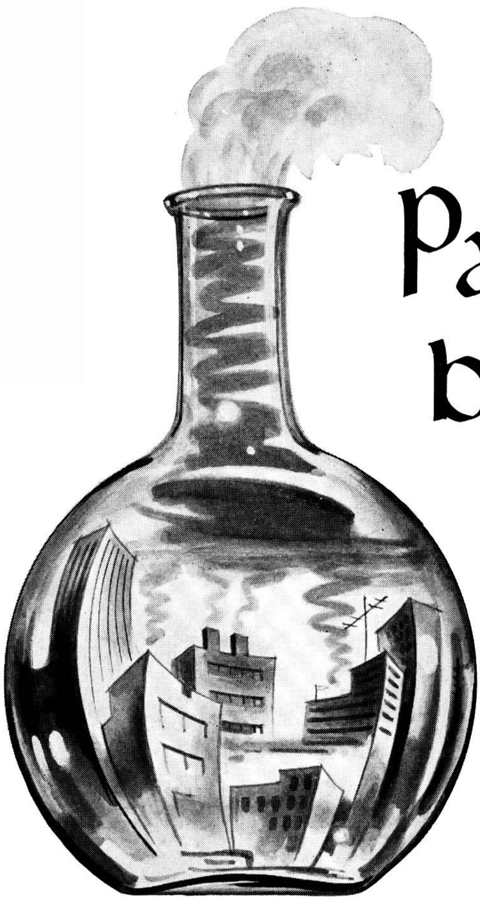

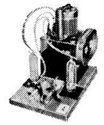

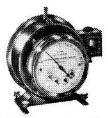

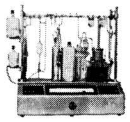

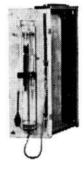

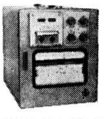

EDITORIAL

Environmental facts obscure the truth

In a sophisticated, highly technological society there seems little need to dally at the task of cleaning up the environment

ENVIRONMENT is a dirty word. It needn't be. It could be an 11-letter word that conjures up some pretty fine thoughts. But to the housewife it means dirtier linens and drapes. To her husband it means extra paint jobs that keep him from his weekend golf. To the sportsman it is a fish story that ends with disappearance of sport fish and appearance of trash fish if, indeed, any fish appear at all.

There can be little doubt about the callous attitude of the members of our society, individually and collectively, as they go about fouling the environment. Industry is a handy scapegoat because of its general reluctance to admit to doing anything that could possibly contribute to pollution. According to industry, some of the smells and particulates may be troublesome, but they're harmless. The water temperature might be up 15 degrees, but the river doesn't freeze in winter. Besides, if industry has to clean up, the effect could be economic ruin and abandonment of the offending town by industry.

But the individual in our society is much to blame, also. His city sewers dump untreated sewage into rivers because he votes down bond issues for new facilities. His concern for solid waste disposal at five pounds per person per day ends at the garbage pail at the curb. His car contributes heavily to air pollution (more than half of all air pollution comes from cars). In a society that bought close to 2 million air conditioned cars last year—at a cost of more than $300 per car for air conditioning—there is little doubt of a compulsion in that society to seek relief from its environment.

All in all, this is a sad commentary on a society that has the technology and the resources to take great strides in solving the major portion of its pollution problems. True, not all the problems can be solved or even all the problems known. But we certainly know enough to take some giant steps now. There seems hardly any justification in waiting until we know everything. Man just isn't built that way. And there is no reason to begin changing him when it comes to dealing with his environment.

The carelessness and indifference of man should not be allowed to blight the environment. This is the place where we dwell. And to the extent which we defile and destroy the environment we place limits on our right to live a full life or to look at the positive face of health, as the quality of individual living was described by Dr. William H. Stewart, Surgeon General of the U.S., in recent testimony at a Senate hearing (ES&T, April, page 271).

When the environment has changed, living things have adapted, moved away, or perished. Geologic history is replete with examples. But we need not look back; we need only to look around us.

Environment is a generic description of something that is one thing in Atlanta and another thing in Zanesville. It is an invigorating experience in the cool of a forest evening, an enervating experience in the close, stifling heat of a big city night. The fact is the environment is many things. The truth is the environment is one thing: the place where man lives. The fact should not be allowed to obscure the truth.

Melvin J. Josephs

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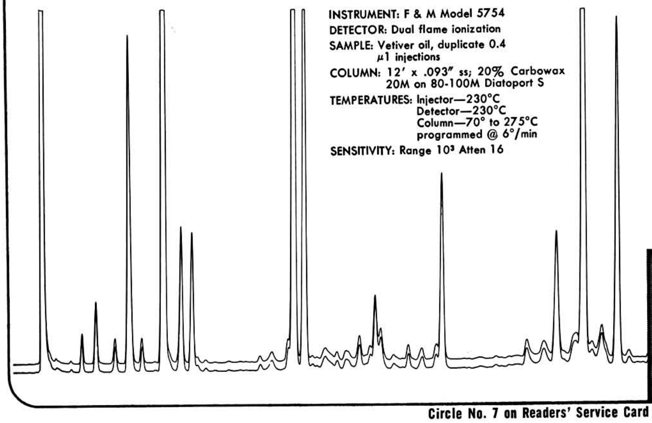
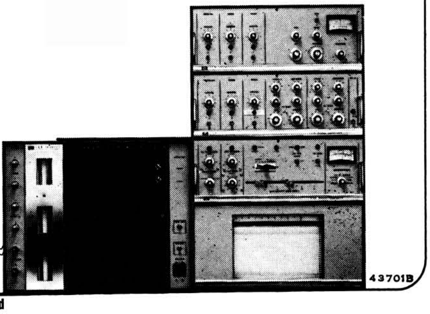


INSTRUMENT: F & M Model 5754
DETECTOR: Dual flame ionization
SAMPLE: Vetiver oil, duplicate 0.4 μl injections
COLUMN: 12′ x .093″ ss; 20% Carbowax 20M on 80-100M Diatoport S
TEMPERATURES: Injector—230°C
Detector—230°C
Column—70° to 275°C programmed @ 6°/min
SENSITIVITY: Range 10^3 Atten 16



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ENVIRONMENTAL CURRENTS

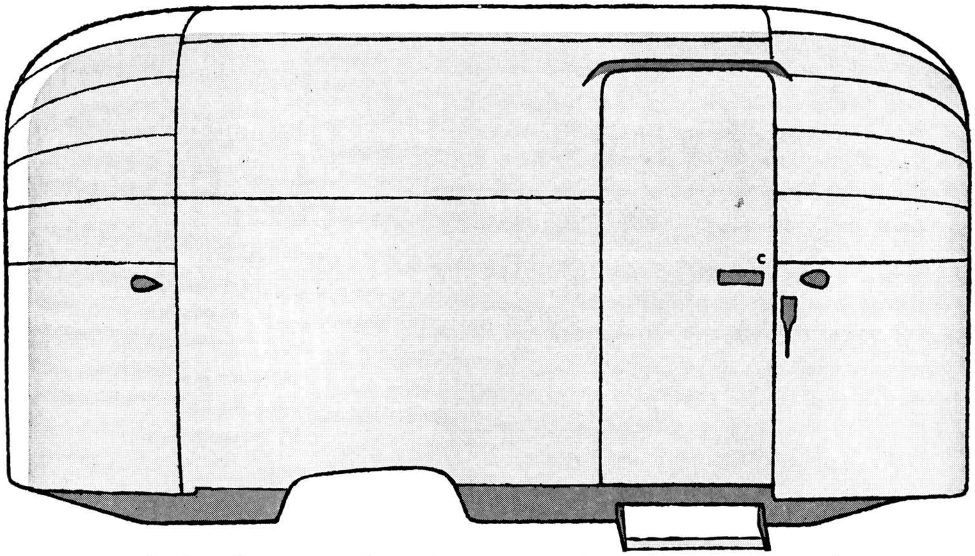
Federal Air Pollution Control Legislation

The Senate Subcommittee on Air and Water Pollution wound up its hearings on the Air Quality Act of 1967 (ES&T, February, page 206). During three months of hearings, the subcommittee heard various industry spokesmen, while insisting they supported some type of legislation, attack almost every section of the Administration's proposals. However, the favorite target seemed to be the proposal giving the Secretary of HEW authority to set national uniform emission standards for certain industries. The Manufacturing Chemists Association said such standards "serve administrative convenience only"; they are "scientifically untenable and may be economically wasteful." In a specific area, a sufficient number of individual plants could produce an unsatisfactory ambient condition. The tendency, says MCA, would be to set standards to handle the worst situations.

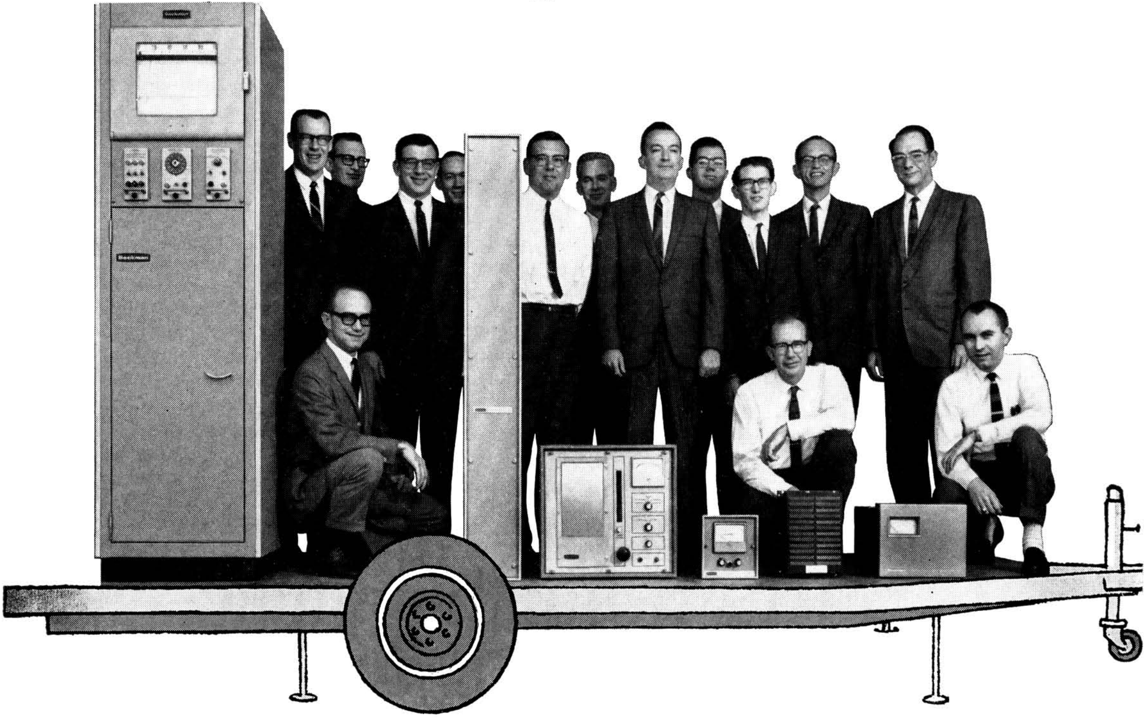
"We hold no brief," says MCA, "for the complaint of unfair competitive advantage when air pollution control regulations differ for similar operations in different regions. Other cost elements are not equalized, nor should they be. Uniform emission standards would be as disruptive to competition in some instances as they might work favorably in others." MCA believes ambient air quality standards should be used as the primary basis for air pollution control. This approach, contained in an amendment to the legislation, is similar to the pattern of standards development used for water pollution control.

But before standards can be set, air quality criteria must be determined, and, again, the subcommittee heard objections. PHS, which is developing the criteria, has so far released criteria for only one pollutant—sulfur oxides. The National Coal Policy Conference, Inc., said that HEW has "tried to establish impossible standards in relation to our principal pollutant," and that the result would be to put the industry out of business in many cities. Under intensive questioning by subcommittee chairman Sen. Edmund Muskie (D.-Me.), HEW's John T. Middleton admitted that little work has been done on pollutants at or below concentrations to which the population may be exposed—even in the case of sulfur oxides, where, for the most part, short term, high concentration studies have been run.

In the course of the hearings, the American Petroleum Institute, the Edison Electric Institute, and the American Paper Institute opposed nationwide emission standards, as well as other provisions of the legislation. Near the end of the hearings, Sen. Muskie, a key figure in much of the recent pollution legislation, appeared to be skeptical about the nationwide standards idea. The bill will now be considered by the Public Works Committee, then by the Senate and House. The legislative mill grinds fine, and probably no air pollution control bill will come out of Congress this year.



A successful air monitoring station is more than a trailer



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ENVIRONMENTAL CURRENTS

Pleasure Boats and Pollution

No sewage treatment device, no boat permit—this is the Tennessee Valley Authority's edict to boat owners who intend to use Norris Lake after July 1. The edict, which may be extended to other TVA lakes, requires that each boat or floating structure have a certified statement showing it is equipped either with a state-approved treatment device properly installed or has no toilet facility of any kind. While some boating enthusiasts consider the water pollution from small boats slight in the total picture, others do not agree. (Pleasure boats numbered 3.5 million in 1950 and 8 million in 1965.)

Since 1957, 28 states have enacted boat pollution laws. The laws vary widely, posing problems for the boat operator who plies the waters of more than one state.

The types of sewage management devices available for small boats is just as diverse. The oldest and simplest type is the holding tank. Also available are incineration units fired by bottled gas. These units do the most complete job of waste disposal, according to *Chemical and Engineering News* (May 8, page 35). A number of chlorinator-macerators are now on the market; some use calcium hypochlorite tablets, others liquid hypochlorite solution (household bleach). Another unit is a colloid mill-iodinator.

Thomas F. Kelleher, of the Federal Water Pollution Control Administration, says that "the biggest need in the field of sewage treatment devices for boats is for some large corporations to realize that there's profit to be made here. I don't think we've seen the last word in treatment ideas. Large companies, with money for R&D and know-how, could probably make some major technological breakthrough and corner a large segment of the market."

Atmospheric lead pollution and gasoline manufacture

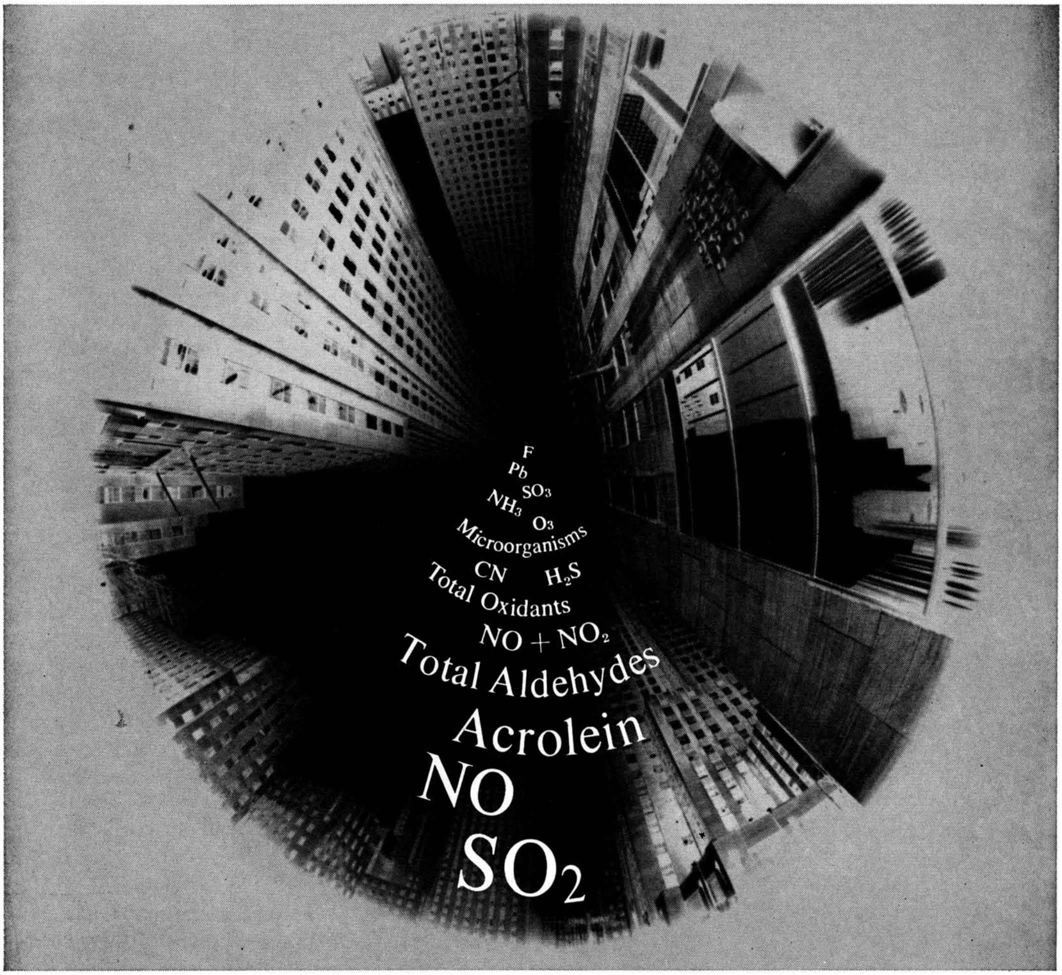
As part of the broad research program on air conservation, the American Petroleum Institute has started a variety of projects aimed at developing data on the use of lead additives in gasoline. According to a report by Bonner & Moore Associates for APT, making lead-free gasoline equivalent in antiknock quality to current gasoline would, with present technology, require the refining industry to spend $4.24 billion for new process units. The average cost of manufacturing would increase by slightly more than two cents per gallon which, at present levels of purchase, adds up to $1.5 billion per year, attendees at API's division of refining 32nd Midyear meeting in Los Angeles (May 16) were told. Furthermore, producing such gasoline would require 5% more crude (500,000 barrels per day) than current processes and 50 times more platinum than the industry currently uses.

Making Water for Peace Permanent

The U.S. is setting up a Water for Peace Office to lead and coordinate the country's efforts in the world's water programs. In his welcoming address to the International Conference on Water for Peace (Washington, D.C., May 23–31), President Lyndon B. Johnson also called for creation of regional water resource centers throughout the world to provide leadership and stimulate cooperation among nations. The President would like to see two such centers in operation within two years, and pledged the U.S.'s willingness to provide "our fair share of the expert assistance, the supplies and equipment, and the financing."

Specific air pollutants: their detection and quantitation

Monitor AutoAnalyzer®: the only automatic instrument that provides a profile of air contamination through the specific wet chemical procedures of the USPHS



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ENVIRONMENTAL CURRENTS

Feds Apply Existing Air Pollution Law

The Government is using the legislation already on the books, calling the first public hearings under the Clean Air Act of 1963. Accused of interstate air pollution is the Bishop Processing Co., which operates a plant for rendering chicken and fish parts into tallow and animal feed. The plant, located in Maryland, is sending "sickening and nauseating odors" to Selbyville, Del., a short distance away.

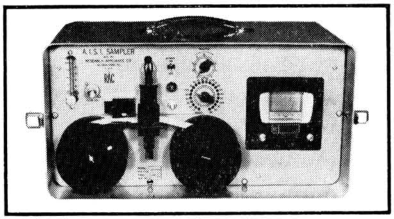
At an informal conference in September 1965 (also the first called under the act), HEW ordered the company to take abatement measures. The hearing (the second phase of the enforcement procedure) was called when officials concluded the company had not complied. The company maintains it has spent substantial sums for odor control and reduced its major odor-producing operations, but that it hasn't been able to get clear recommendations from officials about how to control the odor or to what level the odor must be reduced. The company also says that after it took control measures, the Maryland Department of Water Resources complained that the plant's air pollution control devices, which use water, were polluting streams. An HEW engineer who inspected the plant said the equipment was inadequate to control odors from decaying and processed animal matter, that little attempt was made to keep the premises clean, and that storage facilities leaked. The five-man hearing board recommended that HEW order the company to curb the offensive odors by December 1 or face prosecution.

Decomposing solid waste by composting

The availability of nitrogen in waste materials may be the limiting factor in their decomposition, says Dr. David T. Knuth. Dr. Knuth is in charge of a study of the chemical reactions that occur during the decomposition of solid municipal wastes such as those found in dumps, landfills, and incinerators. The research is being conducted at Battelle Memorial Institute's Columbus Laboratories under a grant from the Office of Solid Wastes, U.S. Public Health Service. Dr. Knuth uses a specially designed and hand-fabricated fermentor, which is equipped with agitators that permit air to enter from the bottom of the vessel and maintain close contact with the waste particles. The fermentor facilitates studies on a scale between "bench top" and pilot plant, and can be applied to a wide variety of studies involving the fermentation of solids.

Trash trains—the unit train that could

Trash trains are the newest twist in solid waste disposal. The Public Health Service has awarded $178,200 to the American Public Works Association as the downpayment on a three-year project expected to cost a total of $468,800. The PHS grant was made to "investigate the feasibility and cost benefits of transportation of refuse and other solid wastes by rail from cities to abandoned strip mines and other land in need of reclamation." Cost of the project will be shared by the New York Central Railroad system and cooperating cities throughout the country. The unit trash train project, announced early this month, fits nicely with the three-year demonstration project announced earlier this year (ES&T, January, page 11) in which Maryland and PHS planned to test the feasibility of using abandoned strip mines for solid waste disposal.



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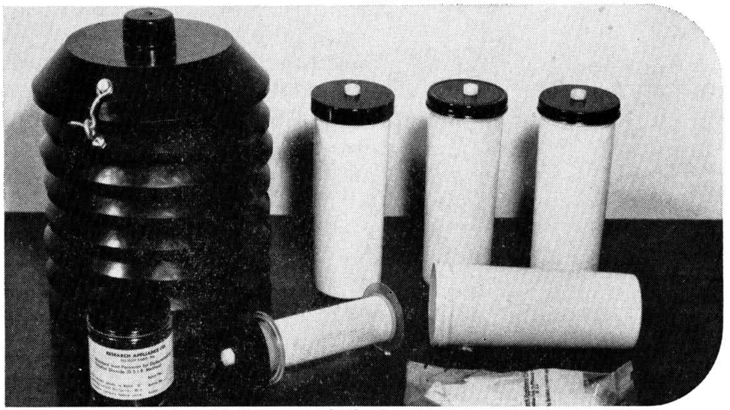
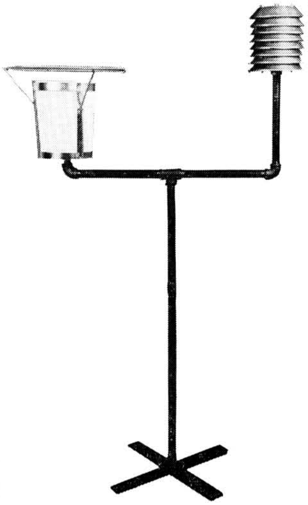
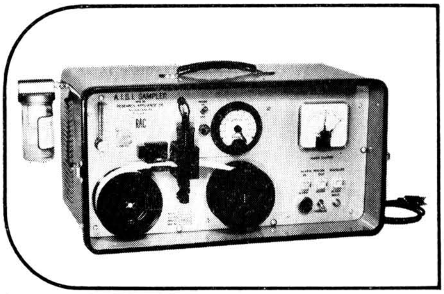


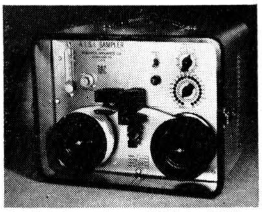
Lead Peroxide Instrument for Monitoring Sulfur Dioxide—$50.55/Station.



Dust Fall Stanchion with Jar and
SO_2 Station $54 less SO_2 shelter.



Hydrogen Sulfide Alarm Sampler—$1400.



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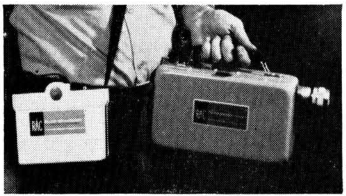

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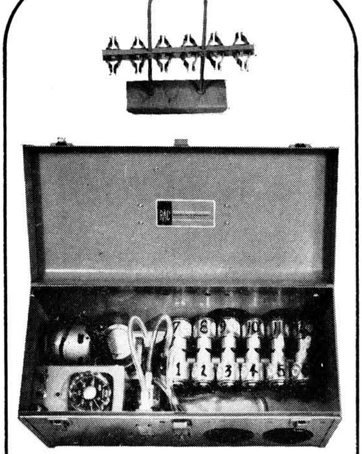


Sequential Sampler—$400 to $570.

ENVIRONMENTAL
CURRENTS

State Water Quality Standards Not Yet Acceptable

Most states will meet the June 30 deadline for submission of water quality standards, James L. Agee and Allan Hirsch of the Federal Water Pollution Control Administration told attendees of the 22nd Annual Purdue Industrial Waste Conference (May 2–4). And, despite the fact that no state has yet submitted a standards program that is fully acceptable to the Secretary of Interior, Agee pointed out that at least a half dozen programs will have been accepted by midsummer. Goal for completion of the acceptance steps for all state programs is September 30. Although South Dakota and Iowa are likely candidates for early acceptance, both Illinois and Indiana are considered dark horse possibilities.

Adoption, implementation, and enforcement of water quality standards will have a profound effect on future water pollution control programs and will put heavy emphasis on water quality monitoring, secondary or tertiary treatment for municipal wastes, adequate treatment of industrial wastes, efficient operation of municipal and industrial waste treatment plants, and the development of programs leading to the control of pollution from vessels and marinas, land erosion, agricultural drainage, mine drainage, and other nonpoint sources, Agee and Hirsch said.

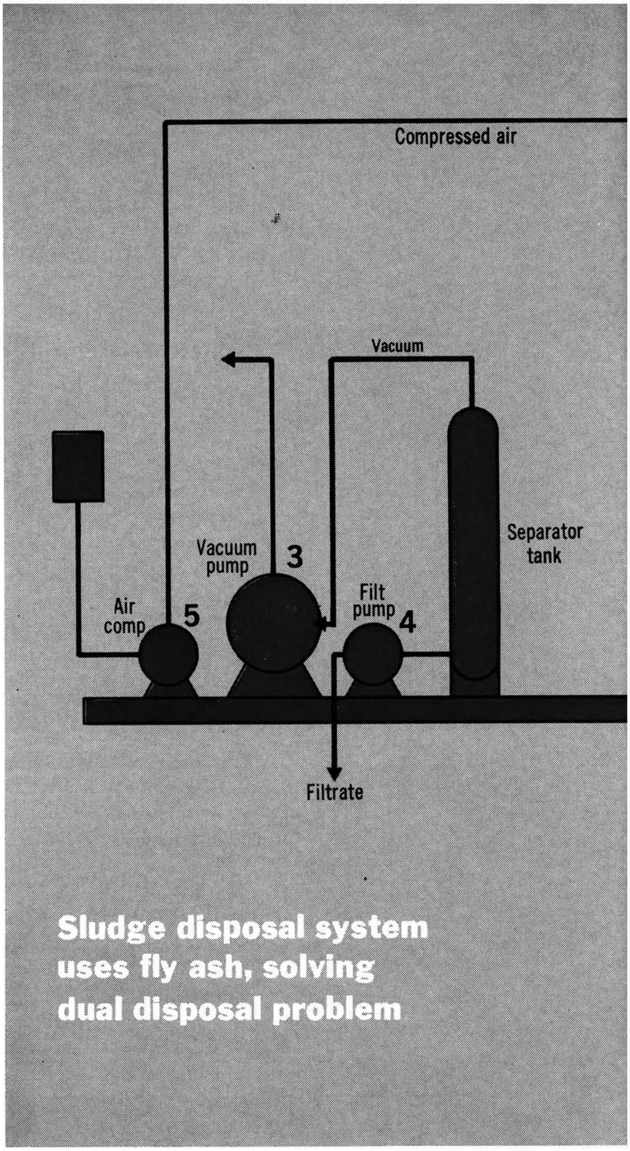
Fuel cell controls stack emissions

Emissions from stacks are controlled and furnace efficiency is enhanced by the use of a fuel cell control device, still in the experimental stage, built by Westinghouse. Operation of the control is based on the fact that oxygen flowing through the zirconium oxide solid-electrolyte fuel cell generates an electric current. The cell, placed in the furnace flue, monitors the oxygen stream in the flue. Increased oxygen in the flue gases means increased air, a cooler-than-desired furnace temperature, and, most likely, smoke emission from the stack. Decreased oxygen implies incomplete combustion and the emission of carbon monoxide and unburned by hydrocarbons. The fuel cell responds to the various oxygen levels with a proportional electric signal that, in turn, goes to a control that regulates the feed rate of air and fuel to the furnace, adjusting these rates to preset, optimum levels.

Eddies

The theme of Willing Water Week (August 13–19) is "Water Is Happiness" . . . Weighted tires are dumped on reefs off the Florida shore, solving a disposal problem while adding to the stability of the reefs. . . Oak Ridge National Laboratory has developed a roller-shaped device that sits on the ocean floor in the littoral zone and records rate of movement, direction, and volume of radioisotopically tagged sand. . . From the Water for Peace conference comes the news that engineers of classical Rome constructed 359 miles of aqueduct to provide 50 gallons of water per day to each citizen, whereas 17th century Paris provided only 2½ quarts. . . Also the information that 97.2% of the earth's water is stored in the oceans and more than 2% is frozen in icecaps and glaciers. Of the less than 1% remaining, 0.6% is underground, the water in streams and lakes accounting for what's left. Only 0.001% is distributed throughout the atmosphere.

OUTLOOK



Sludge disposal system uses fly ash, solving dual disposal problem

Fly Ash Aids in Sludge Disposal

Waste by-product from power generation facilitates sludge dewatering and thus helps to solve two disposal problems at once

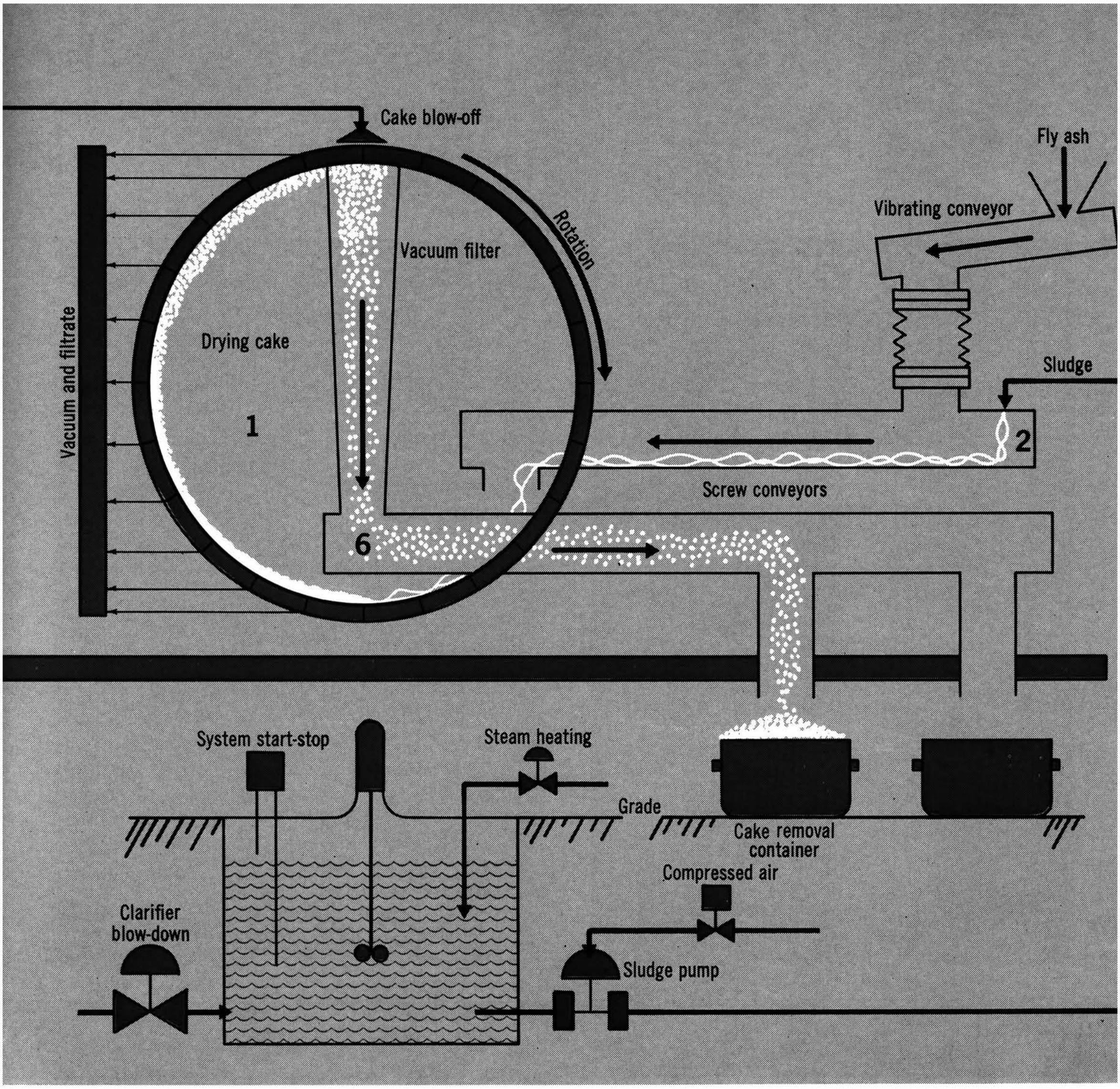
Fred W. Moehle
Uniroyal, Inc.,
Mishawaka, Ind. 46544

Dewatering industrial waste plant sludge using fly ash as a filtering aid has proved successful at the Uniroyal, Inc., plant located in Mishawaka, Ind. This treatment plant, located on the St. Joseph River, was put into operation in December 1964. It is designed to handle only contaminated industrial waste; all sanitary waste is discharged to the city sewer system.

To fully understand where the sludge comes from, how it is collected and how dewatering is accomplished, it might be well first to describe the entire waste treatment plant operation. Briefly stated, this facility can be considered a filtration plant accomplishing its objective by means of chemical filtration as opposed to mechanical filtration.

Upon entering the plant the industrial waste is deposited in an equalizing basin. From the equalizing basin the waste is pumped to a weir box which is at the highest elevation in the treatment process. The waste flow through the clarifying process, therefore, is accomplished by means of gravity. From the weir box the waste water flows through the first stage mixing tank where Ferri-Floc (ferric sulfate), a flocculating agent, is added.

The waste then flows through the second stage mixer where a small amount of Separan, a flocculating aid, is added. Passing from this tank the waste water enters the first stage flocculator where a high speed mixer brings the Ferri-Floc into intimate



Sludge dewatering

In the process of dewatering the sludge, six major pieces of equipment are involved.

The filter drum **(1)** *is a 10-foot in diameter × 5 foot deep rotating cylinder with an internal lining of 20 sectionalized vacuum chambers. The internal surface of each vacuum chamber is perforated with holes about one-sixteenth inch in diameter. Over each perforated plate is installed a nylon cloth, caulked in place with manila rope. Space is provided around each chamber to receive the caulking rope. A timing valve sequenced with the rotating drum allows vacuum to be admitted to the chambers as they approach the top of the drum. When, in turn, each chamber reaches the top of the drum, the vacuum is shut off and compressed air is admitted to the chamber.*

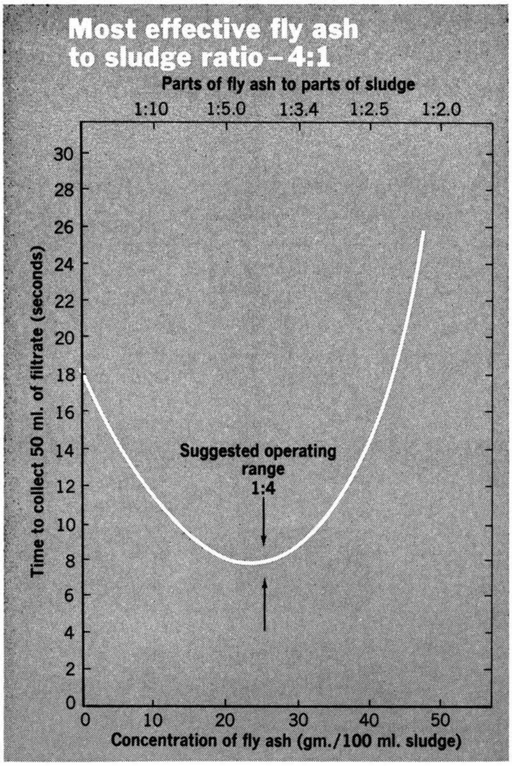
The sludge feed mixing conveyor **(2)** *is a screw conveyor having a 9-inch diameter screw with folded flights. This conveyor is used to transport and mix the sludge-fly ash mixture to the filter drum.*

A centrifugal blower **(3)** *is used to maintain the desired vacuum in the filter drum vacuum chambers. This blower takes its suction through a vacuum receiver or separation tank. The filtrate from the filter drum is separated from the air in the separation tank.*

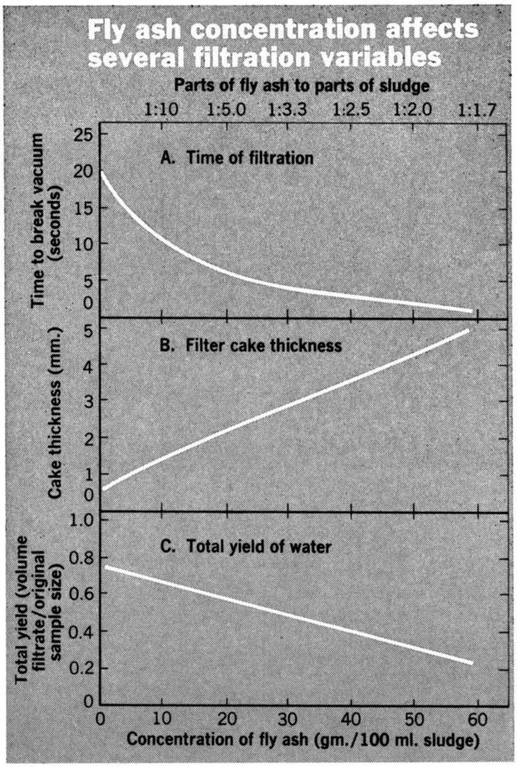
The filtrate pump **(4)** *removes the water which collects in the separation tank and discharges back into the equalizing basin.*

A blower type air compressor **(5)** *supplies air to the vacuum filter for filter cake removal.*

The cake collecting chute **(6)** *protrudes into the upper part of the filter drum to collect the cake discharging it to the cake conveyor for transporting to the dry sludge removal container*



Most effective fly ash to sludge ratio—4:1



Fly ash concentration affects several filtration variables

contact with the various waste particles entrained in the water.

From the first stage flocculator, the water enters the clariflocculator which, in effect, is the second-stage flocculator located in the center of the clarifier. In the second-stage flocculator, a slow moving mixer allows the floc to form and precipitate down through the bottom of the flocculator together with the water in which it is entrained. The clear water rises into the clarifier portion and is allowed to flow over a weir plate around the periphery of the clarifier.

The floc, which settles at the bottom of the tank, is referred to as sludge. The sludge build up in the bottom of the clariflocculator is periodically allowed to flow or is blown down into a sludge collecting tank. The blow-down is set on a time basis by the plant operator who decides on the time setting after daily checking the level of the sludge blanket by means of a sampling bottle.

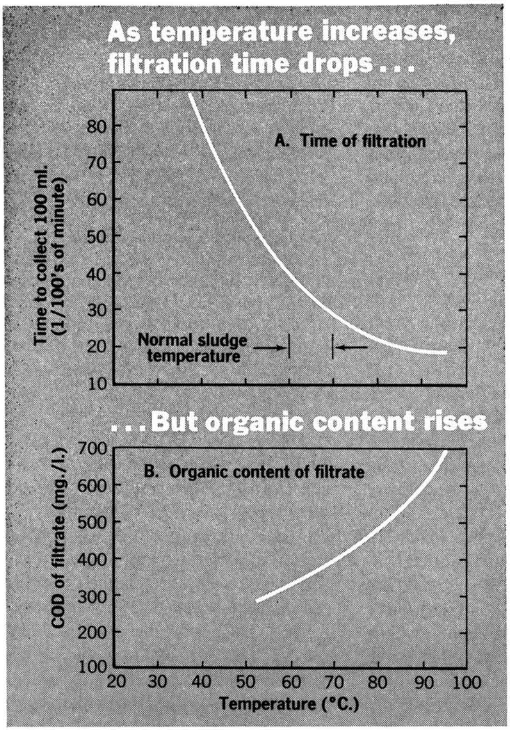
It is the purpose of this article to expound on the method of dewatering this sludge using fly ash as a filtering aid.

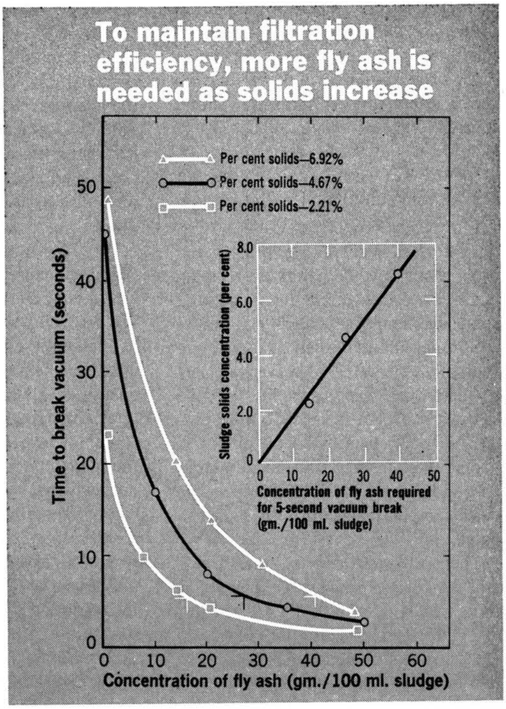
System operation

The sludge from the clariflocculator is collected in a 27,000-gallon concrete sludge holding tank located below grade. Within the tank are a motor driven agitator to keep the solids in suspension, a steam heating pipe to maintain a sludge temperature of 150° F., and a level controller to start and stop the dewatering process. Sludge is pumped from this tank to the feed end of the sludge feed mixing conveyor. The pumps are positive displacement diaphragm types with a controlled compressed air impulse admitted to the top of the diaphragm. The air impulses are controlled by a timer which provides a means of increasing or decreasing the number of air pulses. In this way the output of the pumps can be controlled.

Fly ash is introduced approximately 10 inches downstream from the point at which the sludge enters the top of the sludge feed mixing conveyor. The fly ash is obtained from a 34.5-foot high × 18-feet diameter ash storage silo located next to the treatment plant. All the ash from the burning of pulverized coal for steam generation at the power house is deposited in this silo. Roughly 30% of the ash from the power plant is used in the sludge dewatering process.

Fly ash is transported from the silo to





the sludge feed mixing conveyor by means of a vibration conveyor. The oscillating frequency of this conveyor can be varied by means of a small crank and in this way the ash feed rate can be controlled.

The sludge feed mixing conveyor (a screw-type conveyor with folded flights for mixing) mixes and transports the fly ash–sludge mixture a distance of 8 feet. This conveyor discharges into the rotating vacuum filter drum. Tests have shown that the optimum mixture should be in the range of four parts sludge to one part fly ash by weight, although this proportion will vary depending on the solids content of the sludge. Our operating practice has been to adjust the sludge–fly ash mixture as determined by visual observation.

Since the rotating vacuum filter drum is powered through a variable speed drive, the drum rotation speed can be varied. Drum speed is adjusted according to the cleanliness of the filter cloths and the cake thickness. Usually, the drum speed may be adjusted to rotate between 0.09–0.192 r.p.m. However, this speed changing is not a continuous adjustment.

Dewatering

Dewatering starts when the mixture enters the filter (about 12–18 inches depth of mixture is in the bottom of the filter at all times). The mixture continues to dewater, forming a cake on top of the cloth until each vacuum section, in turn, revolves to the top of the drum. Because of a 15–20 in. Hg vacuum in the chambers beneath the cloth, the water (filtrate) is filtered out into the vacuum chamber. The filter is capable of dewatering up to 10 gallons per minute of sludge.

When a vacuum chamber rotates to the top of the drum, the vacuum is automatically shut off and compressed air at 3 p.s.i.g. is introduced to the chamber. The compressed air behind the cloth dislodges the cake which then falls into a collecting chute. The chute directs the cake to a screw conveyor which transports the residue to one of two containers. When full, these containers are trucked to the disposal area. The dewatered sludge has no discernible odor.

The filtrate which collects in each of the vacuum chambers is directed from the chamber by means of a pipe connected to a multiport valve. The multiport valve permits the revolving pipe arrangement to be connected to stationary piping. The filtrate and air taken through the filter cloth passes into a separation tank. The filtrate collects in the bottom of the tank and is pumped by means of the filtrate pump back to the equalizing basin. The air passes out through the vacuum pump and is released to atmosphere.

Sludge conditioning

In order to properly dewater this industrial waste plant sludge, which is approximately 62% inorganic (mostly lamp black, clays, vinyl and ferric sulfate), some operating parameters had to be established. Prior to plant construction, trials and tests were undertaken not only to determine the feasibility of the scheme, but to set specifications for purchase of equipment. After the plant was in operation, further field and laboratory tests were conducted to determine if the dewatering system performed as anticipated.

These investigations considered several variables on the sludge dewatering process:

- The proper concentrations of fly ash
- The effect of sludge temperature on the dewatering process
- The effect of hydrogen ion concentration of the sludge (pH)
- The effect of sludge solids concentration
- The effect of various vacuum conditions for proper sludge dewatering

The trials were conducted in a laboratory using sludge and ash samples obtained from the operating plant.

Fly ash concentration. One of the first studies was to check the fly ash–sludge ratios. In this test only the fly ash concentrations were changed; all other possible variables were held constant. The applied vacuum was maintained at 29 inches Hg, the sludge temperature at 65° C. and the per cent sludge solids at 4.67%—in all tests a 100-ml. sludge sample was used. The results of these trials were plotted.

Of particular interest was the time required to collect one half of the original sample's volume (50 ml. filtrate from 100 ml. sludge sample) for various concentrations of fly ash. Increasing fly ash concentration improves the rate of filtration until a concentration of about 25 gm./100 ml. (4 parts sludge to 1 part fly ash) is reached. Increasing the fly ash concentration beyond this point decreases the rate of filtration. From these observations we conclude that initially increasing the concentration of fly ash serves to give the filter cake a more rigid structure and provides avenues of flow for the water to be withdrawn.

With no fly ash added, the sludge is very compressible and in the presence of a vacuum the filter mat becomes clogged. With fly ash concentrations above the 4 to 1 ratio, however, a large portion of the water is taken up by the fly ash; consequently, it takes an increasingly longer time to withdraw the 50 ml. of filtrate.

Although the data clearly demonstrate the value of the 4 to 1 ratio, the data are not, perhaps, as representative a property of filterability as the time required to break vacuum. These data again demonstrate that above the 4 to 1 (25 gm./100 ml.) ratio, an additional concentration of fly ash does not appreciably improve the filterability of the mixture. As would be expected, the greater the quantity of fly ash added to the sludge, the greater will be the thickness of the filter cake. This relationship is linear.

The final interesting observation in this series is related to the effect of adding fly ash to the sludge and the effect on total yield of water. Data from these studies clearly show that the filtrate yield decreases linearly with increasing fly ash concentrations. For example, without the addition of fly ash (although it will take a relatively long time), the maximum amount of water which can be withdrawn from the sludge under these conditions is 80%. Of course, to obtain this 80% yield the vacuum filter requires an extremely short operating cycle between cleanings, since the filter mat becomes clogged or blinded in very short order. As fly ash is added in increasing amounts, the amount of water withdrawn decreases in direct proportion, reaching a value of about 20% when 60 gm./100 ml. (1.7 to 1 ratio) of fly ash is reached; the final amount, no doubt, has been absorbed by the fly ash.

Fred W. Moehle *is chief power engineer at Uniroyal's manufacturing facility in Mishawaka, Ind. He is also vice president of Michiana Watershed, Inc., a nonprofit organization directed to the beautification of the St. Joseph River valley. And he is a member of the Indiana Water Pollution Control Association from which he holds a Certificate of Competency. Mr. Moehle served 8 years in the U.S. Navy (1937–45) as a Chief Water Tender. He is a graduate of Pratt Institute, Evening School of Science and Technology, Brooklyn, N.Y. (1950). Before joining Uniroyal (1956), Mr. Moehle was power plant superintendent for Panama Power and Light Co. in the Republic of Panama (Ebasco International Corp.) for the period 1952–56.*

Sludge temperature. The next series of trials was conducted to determine the effect of sludge temperature on the dewatering process. As a result of the previous trials, the optimum fly ash concentration of 25 gm./100 ml. (4 to 1 ratio) was selected for all remaining tests. In this series, the applied vacuum again was held at 29 inches Hg, the per cent sludge solids at 4.67%. A 100-ml. sludge sample was used in all cases. Only the sludge temperature was varied. As the sludge temperature increases, the time required to remove the filtrate decreases. However, after a temperature of 70° C. (158° F.) is reached, the improvement in filtration is very small with increasing temperature.

In further temperature studies, we noted that as the temperature of the sludge increases, it serves to put an increasing amount of the organic sludge into a soluble form. This results in a higher chemical oxygen demand (COD) in the filtrate. As a result of these two relationships, a sludge temperature of 65° C. (149° F.) seems to us the most desirable both with respect to the rate at which the sludge can be dewatered as well as the amount of organic material which would otherwise pass into solution at higher temperatures.

Hydrogen ion concentration (pH). The effect of the sludge pH on the dewatering process was studied since pH can often have a marked affect on a vacuum filtration process. In these studies all other variables (that is, ash concentration, sludge temperature, sludge solids, and vacuum) were held constant at the values stated previously while the pH was varied from 2 to 10. The pH value of the sludge filtered in our process appears to have very little effect on the sludge dewatering system. We attribute this to the choice of fly ash as a sludge conditioner in place of some highly chemically reactive and pH dependent chemical substance as a sludge conditioner.

Sludge solids concentration. Realizing that the solids concentration of the sludge would no doubt have an effect on the dewatering ability of the filter, trials were undertaken to determine to what extent our process would be affected. Three sludge samples were used, each with a different solids concentration: 2.21% solids, 4.67% solids, and 6.92% solids. All other possible variables were held constant with the exception of fly ash. Fly ash was added to each sample in varying amounts, ranging from 0 to 50 gm./100 ml. We then plotted fly ash concentration against time to break vacuum, which, as stated previously, is a measure of filterability of the mixture.

In all these instances, after a vacuum break time of 5 seconds is reached, additional fly ash concentrations do not appreciably improve the filterability. However, an increase in sludge solids concentration does necessitate a greater proportion of fly ash. A solids concentration of 2.21% requires 15 grams of fly ash per 100 ml. sludge (1 to 6.7 ratio), a solids concentration of 4.67% requires 28 grams of fly ash per 100 ml. sludge (1 to 3.6 ratio), and a solids concentration of 6.92% requires 40 grams of fly ash per 100 ml. sludge (1 to 2.5 ratio). The fly ash concentration, thus, should be adjusted to the sludge solids concentration.

Effect of vacuum. The final trial concerned itself with the effect of vacuum on dewatering process. In this investigation, the vacuum was varied between 0 to 29.25 inches Hg—all other items remained constant. The greater the applied vacuum the shorter the time required to break the vacuum. However, after a vacuum of 20 inches Hg is reached there is no appreciable reduction in vacuum break time. More significant, perhaps, is that the yield of water (filtrate) expressed in per cent (volume of filtrate divided by the initial volume of sludge sample) increases with increased vacuum until a vacuum of 15 inches Hg is reached. At that point (68% water removed), any additional vacuum does not appreciably remove any additional amount of filtrate. This is to say, once a vacuum of about 15 inches Hg is applied, the driest filter cake possible will be obtained.

One other characteristic of the degree of the vacuum applied to the filter that we considered is the rate of filtrate yield within the time it took to break the vacuum. As would be expected, the dewatering rate increases with increased vacuum. From these studies we have established that a 15- to 20-inch Hg vacuum is the optimum condition for dewatering our sludge.

Some problems

As discussed previously, this method of using fly ash as a filtering aid for dewatering our sludge has proved successful. Naturally, we do have some operational problems, but they are to a large extent mechanical.

Prior to the waste treatment plant construction, pilot plant studies (carried out over a two year period) in conjunction with other feasibility studies indicated the desirability of locating the treatment plant in close proximity to the power plant, primarily because it is much less difficult to transport the waste water (pumped through an 8-inch pipeline) than it is to transport fly ash. The treatment plant is approximately 1000 feet away from the waste collection area in the factory.

The day to day operation of this dewatering process is mostly an art. However, this art is based, we feel, on firm scientific facts. Normally, the fly ash concentration is held at approximately 4 parts sludge to 1 part fly ash. This ratio must be adjusted, however, depending on sludge solids concentration and may vary as much as from 1:2.5 to 1:6.7. The sludge temperature is held at 150° F. Since we know of no economically feasible way of accurately measuring the fly ash flow to the mixture, and because we have no desirable method of accurately monitoring the sludge solids concentration on a continuous basis, the operator makes adjustments to the mix as determined by his visual observation of the filter operation. The operator has been instructed in the interpretation of the test data and can intelligently adjust for changing conditions.

The vacuum on the filter is not controlled. With clean cloths and a properly developed cake the vacuum pump will develop a 15- to 20-inch vacuum in the filter chambers. A vacuum greater than 23 inches indicates a blinding of the filter cloths. Initially, we found it necessary to change the filter cloths when such blinding took place. This filter cloth change was necessary every six weeks to two months. However, in later operations we found that an acid cleaning of the cloths—with a citric acid solution—prolonged the life of the cloths up to six months.

Needless to say we do have some operating problems, but we feel sure that they will ultimately be resolved. The use of fly ash as a filtering aid has provided us with a means of utilizing one waste product to economically dispose of another.

This article is based on a paper given by F. W. Moehle at the 22nd Annual Purdue Industrial Waste Conference, May 2–4, 1967. Assisting in the preparation of the paper, design of the facility, and collection of data were A. L. Nicolai, Uniroyal (New York, N. Y.), J. W. Chase, Uniroyal (Mishawaka, Ind.), and M. W. Tenney, assistant professor of civil engineering, University of Notre Dame (Ind.).

Industry Has an Important Role in Development of Water Quality Programs

Nicholas J. Lardieri
Scott Paper Co., Philadelphia, Pa. 19113

We are rapidly approaching an important deadline in the field of water quality. I refer to the date of June 30, 1967, by which time the states must submit to the Secretary of the Interior water quality criteria and an implementation plan for all interstate waters. Most of us are aware, through direct participation, of the great activity these requirements of the Water Quality Act of 1965 have engendered.

The state agencies have been doing a remarkable job in meeting their obligations in this matter. Public hearings on criteria have been mostly completed and many states are in the process of resolving the conflicting views of water users prior to the formal submission of the criteria.

Those of us who have been involved in the recently completed Delaware Estuary Comprehensive Study cannot help but feel some regret over the present activity. Our disappointment is that, owing to lack of time, parts of the methodology used in the study for developing water quality criteria for the Delaware Estuary will not be more universally applied at this time. We believe these techniques provide a rational basis for determining the appropriate water quality objectives and program for a given area.

Water quality conditions and objectives are dynamic. Water quality is constantly changing as a result of use and natural causes and objectives altered in accordance with the needs and desires of society. Thus, while a Delaware Estuary–type analysis may be of limited value in establishing our immediate goals the concept can be extremely helpful in guiding subsequent water quality management programs.

This article deals primarily with the role of our Chester, Pa., plant and other industries in the Delaware Estuary Comprehensive Study. The waste treatment facilities at the Chester plant also will be described as they contain a number of unique features.

The mill is located on the Delaware River at Chester, Pa. It produces approximately 800 tons per day of tissue, towels, and other sanitary convenience products on 10 paper machines. The bulk of the furnish is virgin pulp, although there is a 115-ton-per-day bleach plant for processing internally recovered fibers, paper broke, and unbleached pulp. Close to 16.8 million gallons per day of water is withdrawn from the Delaware River for industrial processes.

Pennsylvania Sanitary Water Board requirements

The effluent requirements for Pennsylvania pulp and paper mills since 1950 have been based on raw waste standards. These values were developed as a joint effort between the Pennsylvania Sanitary Water Board and the industry over a 2-year period.

Pennsylvania Sanitary Water Board raw waste standards and effluent requirements for Chester plant

		Suspended Solids			BOD		
	Production	Raw Waste		Allowable discharge	Raw Waste		Allowable Discharge
	(Tons/ day)	(Lb./ ton)	(Lb./ day)	(Lb./ day)	(Lb./ ton)	(Lb./ day)	(Lb./ day)
Paper Mill	800	40	32,000	...	12.8	10,200	...
Bleach Plant	115	16.5	1,840	...	19.0	2,190	...
Total	...	...	33,840	10,150	...	12,390	8050

The raw waste standards state the 5-day BOD and suspended solids per ton of product expected in wastes from well-run plants employing good housekeeping and recovery methods. The use of the characteristics of *normal* raw wastes from various manufacturing processes is based on the principle of comparable effort in waste treatment by various members of a particular industry.

Having established a reasonably attainable standard for raw wastes, the reduction required by the Sanitary Water Board is applied to the normal raw waste for each type of waste rather than to the individual wastes produced by any particular establishment. The paper industry's experience with the operation of this kind of regulation has been very satisfactory. The raw waste standard concept recognizes that pounds of BOD and suspended solids rather than concentration are the significant effluent parameters. The system encourages maximum internal reuse and recovery and is an equitable method of evaluating performance of plants producing similar products. We have been disappointed that the concept hasn't been more widely understood and adopted.

For the Delaware River in the stretch from Philadelphia to the Pennsylvania-Delaware line, the Sanitary Water Board has required primary treatment, which is defined in terms of the raw waste standard as ". . the settleable solids in the plant effluent as discharged to the waters of the Commonwealth shall not exceed 2%; the suspended solids shall not exceed 30%; and the population equivalent shall not exceed 65% of the standard characteristics afore-said."

Water quality standards were developed for the Delaware Estuary Comprehensive Study through the cooperation of industry, private sector, and local, state, and national authorities

Pennsylvania Sanitary Water Board raw waste standards for pulp and paper mills

Type of Product or Process	Population Equivalent Per Ton of Product Based on 5-Day BOD		Pounds of Suspended Solids Per Ton of Product	
	Av. of 3 consecutive operating days	Av. of 8 consecutive operating hours	Av. of 3 consecutive operating days	Av. of 8 consecutive operating hours
(1) GROUP A TISSUE, GLASSINE, PARCHMENT, CONDENSER, ETC.				
Subgroup "Aa": Tissue Paper	75	80	40	50
Subgroup "Ab": Glassine Paper	25	30	15	20
Subgroup "Ac": Parchment Paper	40	45	20	30
Subgroup "Ad": Miscellaneous Papers	25	30	5	10
Subgroup "Ae": Flax Papers—Condenser	375	415	300	350
(2) GROUP B—SPECIALTY GROUP—FIBRE, ASBESTOS, INSULATING, ETC.				
Subgroup "Ba": Fiber Paper	800	850	200	235
Subgroup "Bb": Asbestos Paper	125	185	290	350
Subgroup "Bc": Felt Paper	210	230	60	65
Subgroup "Bd": Insulating Papers	2250	2500	325	350
Subgroup "Be": Specialty Papers	1000	1200	135	160
(3) GROUP C—COARSE PAPER	90	120	35	50
(4) GROUP D—INTEGRATED MILLS				
Subgroup "Da": Wood Preparation	80	100	40	50
Subgroup "Db": Pulp-Sulfite	3000	3500	35	40
Subgroup "Db": Pulp-Alkaline	300	350	20	35
Subgroup "Db": Pulp-Groundwood	115	130	80	85
Subgroup "Db": Pulp-De-inked (Unfilled Stock)	500	650	375	500
Subgroup "Db": Pulp-De-inked (Filled Stock)	400	500	600	800
Subgroup "Db": Pulp-Rag Cooking	1400	1550	475	500
Subgroup "Dca": Bleaching (1) Long Fiber Stock—Multi- or Single-Stage Bleached and (2) Short Fiber Stock—Single-Stage Bleached	60	70	3	6
Subgroup "Dcb": Bleaching Short Fiber Stock—Multi-stage Bleached	165	185	30	35
Subgroup "Dd": Paper Making	100	125	75	85

With respect to suspended solids, these requirements mean that suspended solids discharged to the stream cannot exceed 12 pounds per ton of paper or less than 0.6% of production. Recognizing that a portion of the suspended solids is nonsettleable, we can easily see that this is an extremely rigid requirement. Allowable 5-day BOD discharge is slightly below 10 pounds per ton of paper.

Waste water disposal

Phase I. The waste water disposal facilities at the Chester mill are composed of both suspended solids recovery and strictly disposal units. The system now installed has resulted from continuous research and development starting more than 20 years ago.

Phase I of the system was installed in 1949 and consists of a waste collection system and four Waco precoat vacuum filters, each with a capacity of 1000 g.p.m. The feed to the Waco filters consists of excess filtrate from the vacuum filter savealls on the 10 paper machines. Saveall filtrates prior to treatment on the Waco units are used primarily in consistency regulators, on wire and felt showers, and as vacuum pump sealing water.

The Waco filters are 8 feet in diameter × 14 feet wide with a fine mesh stainless steel wire 32 feet long. Twenty to 25 tons of fiber per day are used as a precoat, and both precoat and recovered fibers are bleached for subsequent manufacturing use. The filtrate is discharged directly to the Delaware River.

Phase II. Following a period of intensive research and development, the Chester plant installed its Phase II facilities in 1960–61. This equipment consists essentially of a 150,000 gallon collection tank, three Permutit flotation units of 2000 g.p.m. each and three Sharples P-3000 Super-D-Canter high speed centrifuges. Because of space limitations, it was necessary to house these facilities on piers extending over the river.

The feed to the Phase II system consists of drainage from process chests and tanks, floor drainage, washup water, seal water, and other miscellaneous wastes. Clarified effluent is discharged to the Delaware River while the float, which normally averages about 2.0% solids, is dewatered on the P-3000 centrifuges which have a capacity of 25 g.p.m. each. The dewatered sludge, averaging about 30% solids, is hauled away for land disposal on a contract basis. Processes for further dewatering and possible on-site burning are under study.

The results in 1966 showed efficiencies below those in previous years. This decline was attributable to several factors, the most important of which were more frequent color changes on the paper machine and a loss of centrifuge efficiency caused by internal wear.

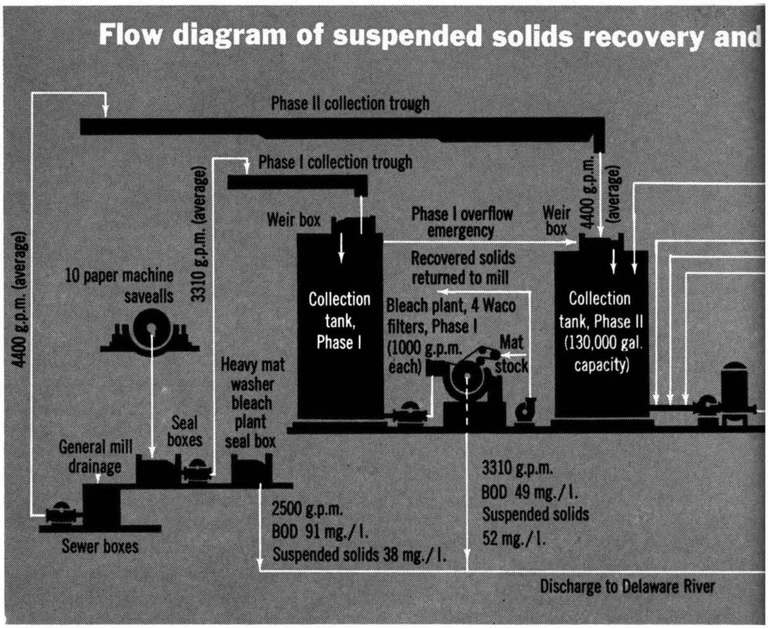
A program to remedy these conditions is now in progress. Its major elements are the replacement of 75-hp. motors on the flotation unit feed pumps with 100-hp. motors and the rebuilding of the centrifuges. The larger pumps will permit more uniform operation of the flotation units during peak flows which result during color changes on the paper machines.

The centrifuge modifications consist of replacing single lead conveyors and associated bronze insert bearings with double lead conveyors and ball bearings. It is anticipated that these alterations will increase the capacity of the individual units from 25 g.p.m. to 40 g.p.m., eliminating occasional sludge tank overflows. An increase in sludge cake density to 35 to 40% is expected, as well as some reduction in centrate solids which are returned to the flotation unit influent.

Costs

The capital costs of the effluent facilities at Chester are as follows:

Phase I	$ 650,000
Phase II	1,250,000
	$1,900,000



Flow diagram of suspended solids recovery and

Waco filter performance (Phase I)

	Flow (Millions of gallons per day)	Suspended Solids (Mg./l.)	BOD (Mg./l.)
Influent	4.8	460	211
Effluent	4.8	56	49
Per Cent Removal	...	87.8%	76.8%

Flotation-centrifuge performance (Phase II)

	Flow (Millions of gallons per day)	Suspended Solids (Mg./l.)	BOD (Mg./l.)
Influent	6.3	400	178
Effluent	6.3	144	76
Per Cent Removal	...	64.0%	57.3%

These are the total actual dollar expenditures at the time of installation and not replacement costs. As previously noted, Phase I was installed in 1949–50 and Phase II in 1960–61.

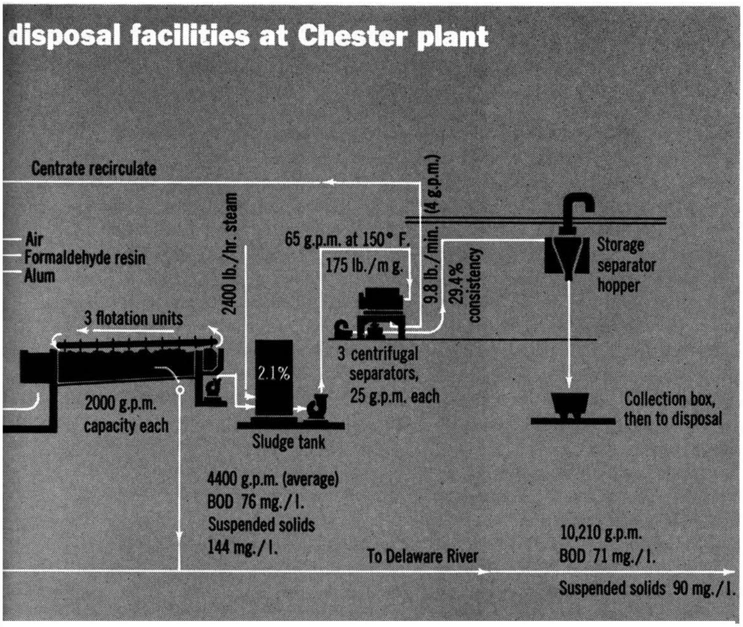
The annual operating costs of the facilities, including labor, maintenance, power, sludge disposal, and fixed charges is $395,000. The fixed charges include interest on capital (5%).

Delaware Estuary Comprehensive Study

The Chester plant, despite its low BOD load to the river, is now faced, together with all other municipal and industrial dischargers of BOD in the estuary, with the prospect of greatly increased removal requirements. These evolve from the Delaware Estuary Comprehensive Study (DECS) referred to earlier.

The study was initiated in 1961 by the Division of Water Supply and Pollution Control of the U.S. Public Health Service (now the Water Pollution Control Administration in the Department of Interior) with the cooperation of the states bordering the estuary, the Delaware River Basin Commission, municipalities, industries, and other water interests. The study developed waste discharge–water quality cause and effect relationships and the total costs for obtaining varying levels of water quality improvements.

The methodology employed by the federal personnel has been reported in depth elsewhere (Thomann, 1963; Thomann and Sobel, 1964). The technique


disposal facilities at Chester plant

Chester plant discharge compared with Pennsylvania requirements

	Suspended Solids			BOD		
	Discharge		Require-ments	Discharge		Require-ments
Source	(Lb./day)	(Lb./ton)	(Lb./ton)	(Lb./day)	(Lb./ton)	(Lb./ton)
Phase I	2,220	...	...	1,940	...	...
Phase II	5,600	...	...	2,970	...	...
Bleach Plant	1,060	...	...	2,440	...	...
Total	8,880	11.1	12.0	7,350	9.2	10.6

involved constructing a mathematical model of the estuary by dividing it into 30 sections. For each of these sections, mass balance equations were written for BOD and dissolved oxygen systems. These equations, in turn, led to two linear differential equations based on the physical, hydrological, and biochemical characteristics. Once all 30 sections were modeled, the result was two systems of 30 simultaneous equations each of which was capable of solution by analog or digital computers.

In order to more firmly establish the validity of the mathematical model employed, the industries participating in the study engaged a consultant, Dr. Donald J. O'Connor, to develop an independent analysis. Dr. O'Connor's report (1966) concluded that the DECS mathematical model and the coefficients developed by the U.S. Public Health Service were reliable and in substantial agreement with his findings.

The views of the estuary community regarding their water needs and desires were obtained through water use advisory committees representing the varied interests of conservation, municipalities, industry, and the general public.

The U.S. Public Health Service conducted an effluent sampling program in 22 municipalities and 22 industrial plants with the combined sources accounting for more than 90% of the waste load to the estuary. The carbonaceous UOD level was found to be approximately 900,000 pounds per day of which 62% was from municipal and 38% industrial sources. It was later established that an additional 900,000 pounds per day of oxygen demand resulted from nitrogenous materials, sludge deposits, and other background sources, the removal of which are not feasible at this time.

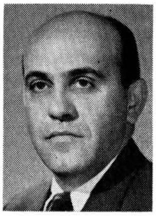
Cost-benefit studies

To enable a cost-benefit analysis, the PHS requested industry to develop, for each source, cost data for facilities to reduce current effluent loads by given amounts. The incremental degrees of waste treatment ranged from 30% to more than 90%. The Chester plant was asked to estimate the capital, operating and maintenance costs of reducing current first stage UOD load by 48, 74, and 92%, respectively. The estimates are based on activated sludge treatment using surface aerators and vacuum filters for final sludge dewatering.

The first condition (48% reduction) would be accomplished by constructing a secondary treatment plant to handle approximately 50% of the total effluent. For obtaining 74% removal of present load—condition number 2—the entire effluent would be given a secondary treatment. To achieve 92% reduction, extended aeration would probably have to be used. The data indicate that operating costs for secondary treatment will add from $320,000 to $474,000 per year to the current cost of about $395,000 per year for primary treatment.

On the other side of the cost-benefit equation, industry was requested to develop estimates of benefits that would accrue to it for various degrees of improvement in estuary water quality. The water quality parameters that were varied individually from present conditions were dissolved oxygen, chlorides, pH, phenols, and turbidity. Depending upon the type, location, sensitivity, and uses of a particular plant, the change may be a positive gain or a loss. The scope of the study included water treatment facilities, distribution systems, process equipment, and waste treatment facilities. Analysis of this type required considerable time and effort by each plant.

The parameter of major significance to the Chester plant is chlorides during low flow periods. We provided esti-



Dr. Nicholas J. Lardieri *is manager of air and water resources for Scott Paper Co. (Philadelphia, Pa.), a position he has held since October 1966. He joined Scott Paper Co. in February 1966, as assistant to the vice president of manufacturing. Previously (1963–66), Dr. Lardieri worked with the Delaware River Basin Commission, of which he was appointed Head of the Water Quality Branch in 1965, and the National Council of Stream Improvement (1956–63). He received his B.S. from Purdue University (1949) in civil engineering and his M.S. (1950) from the same institution. In 1955 he received his Ph.D. in sanitation from Rutgers University. Dr. Lardieri is a registered professional engineer in the states of Pennsylvania, New York, and New Jersey, and a member of the American Society of Civil Engineers and the Water Pollution Control Federation.*

mates on the benefits that would accrue through decreased corrosion if current chloride levels were reduced by fixed amounts. The results from this type of analysis by the industrial group demonstrated that high dissolved oxygen results in serious corrosion problems in cooling water systems which is the major water use of industry in the estuary. The incremental negative benefit (cost) to industry from higher dissolved oxygen shows losses of $15 million—based on present value—during the next 15-year period for the highest of the proposed oxygen levels.

Concurrent with these activities, industry as well as local governments, general public, and recreation, fish, and wildlife interests had subcommittees developing their water use requirements in terms of quality parameters. The quality parameters used to describe these needs in a qualitative nature were acidity and alkalinity and pH; dissolved solids including inorganic, organic color, and odor; floating, suspended, and settleable solids; temperature; and dissolved oxygen.

The industrial water use subcommittee report made the point that for many uses industry must provide water treating facilities suitable to its particular needs. It is, therefore, impractical and erroneous to believe that estuary quality can be upgraded to the point where further treatment for many industrial uses is not necessary. Furthermore, it is far more economical for an industry to treat the volume of water required for its particular purpose than it would be to attempt a similar upgrading of the entire estuary.

Objectives and water use

The summary reports submitted by each of the four subcommittees were subsequently reviewed and condensed by the PHS to five sets of objectives representing incremental differences in water uses and water qualities. The water use goals were generally related to the water quality goals associated with each set. For example, Objective Set I represented the highest water use and also the highest water quality goals. Objective Sets II, III, and IV each represented slightly lower water uses and goals. Objective Set V was equivalent to present conditions. The qualitative differences between the levels were primarily in dissolved oxygen content. In most cases, each quality level would result in average summer dissolved oxygen levels of 0.5 to 1.0 mg./liter greater than the one below it. The higher levels would reportedly increase the probability of anadramous fish passage. For example, federal personnel estimated that at Objective Set II the probability of shad passage in 24 out of 25 years would be at least 90% versus 80% for Objective Set III.

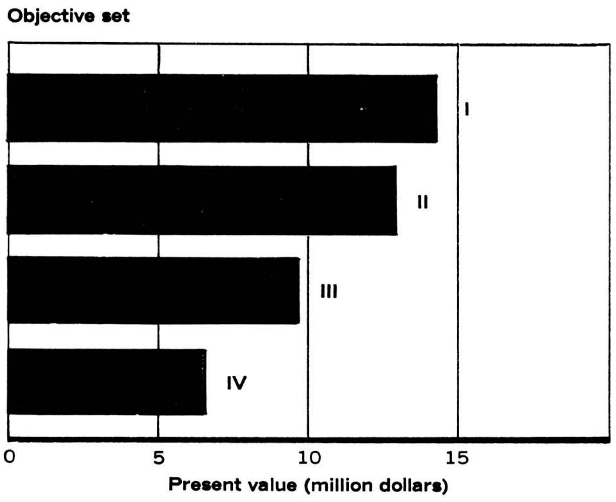
Cost-benefit studies were also conducted by municipal sources and, in addition, estimates made of recreation and fish and wildlife benefits expected from the improved water quality levels. Finally, using the mathematical model which involved both digital and analog computers, the cost for attaining water quality objectives by three methods was determined. These were *uniform treatment*, *zone approach*, and *cost minimization*. *Uniform treatment* means equal percentage reduction in load of all sources. The *zone approach* divides the estuary into three or four zones and requires equal percentage reduction in each zone, but variation between zones to give a lower cost solution. *Cost minimization* means treating or removing lowest cost sources first and selecting the most critical locations in order to give a minimum solution cost to the estuary community for each objective.

The total municipal and industrial

Estimated capital and operating costs for varying degrees of additional treatment at Chester plant

Condition	Effluent UOD (Lb./day)	Per Cent Reduction		Capital Cost (Dollars)	Operating Cost[a] (Dollars per year)	Expected Total Operating Cost (Dollars per year)
		Raw load	Present			
1964 Load	7750	60	0	$1,900,000	$395,000	$ ...
	4000	80	48.4	1,600,000	321,000	716,000
	2000	90	74.2	2,000,000	402,000	797,000
	600	97	92.2	2,600,000	474,000	869,000

[a] Operating costs include maintenance, labor, power, chemicals, depreciation, and cost of capital (5%).



Industrial dissolved oxygen incremental cost in 1964 dollars

costs of achieving the various quality levels under differing waste removal programs differ widely. The costs represent capital costs plus the present value of operating and maintenance costs at a 3% discount rate and a 20-year time horizon. The estimated range of water quality benefits expressed in similar terms for each of the objectives shows similar variety.

It is obvious on studying the data for each objective that uniform treatment is the most expensive of the solutions, a fact which should be considered by the growing number of advocates of nationwide emission standards in environmental control. Also obvious is the fact that the incremental benefits from higher water quality is negligible compared to the additional costs required to achieve it. The ratio of additional costs to benefits is about 10 to 1 in upgrading from quality objective III to II and from II to I. The study's "Preliminary Report and Findings" (1966) issued by the Federal Water Pollution Control Administration contains the following explanation for this finding "... What is apparent from the analyses is that once the water quality reaches a threshold level at which several important legitimate activities may or are assumed to occur, only a small amount of new benefits will result with any additional increase in water quality."

Despite the consensus of water users participating in the study that Quality Level III represented the optimum program at this time, the Delaware River Basin Commission, by vote of 4 to 1, adopted Quality Level II on March 2, 1967. This level requires a BOD removal of at least 85% at all times throughout the estuary. While specific orders have not been issued, it appears that the Chester plant may be required to reduce its 5-day BOD discharge to less than 2000 pounds per day or nearly 2.5 pounds per ton of production. We anticipate that treating this high volume of dilute wastes to such a degree will be extremely difficult to accomplish.

While Scott Paper Co., together with most other water users and waste dischargers, believes that the findings of the study were to a large extent disregarded in the ultimate choice, we remain favorably disposed to the type of analysis that did go on. The concept of attempting to balance costs and benefits of water quality programs and seeking representative views of water users should gain increasing attention as we enter an era in which we must make more efficient use of all of our resources.

Estimated total costs and range of benefits for various water quality levels

(Millions of dollars)

Quality Level	Cost			Range of Benefits
	Uniform treatment	B-zoned	Cost minimization	
I	$490	$490	$490	$155–$355
II	335	275	235	135–320
III	175	155	135	125–310
IV	145	110	100	115–280

Suggested additional reading

"Industrial Waste Manual," Division of Sanitary Engineering Publication No. **14**, Pennsylvania Department of Health, Harrisburg, Pa., March 1, 1966.

Thomann, R. V., "Mathematical Model for Dissolved Oxygen," *J. Sanit. Eng. Div., Am. Soc. Civil Engrs.* **85**, No. SA5, 1–30 (October 1963).

Thomann, R. V., Sobel, M. J.,"Estuarine Water Quality Management and Forecasting," *J. Sanit. Eng. Div., Am. Soc. Civil Engrs.* **85**, No. SA5, 9–45 (October 1964).

O'Connor, D. J., "Water Quality Analysis of the Delaware River Estuary," unpublished report to Industrial Participants-Consultant Project—DECS Industrial Subcommittee of Technical Advisory Committee, April 1966.

"Delaware Estuary Comprehensive Study—Preliminary Report and Findings," Department of the Interior, Federal Water Pollution Control Administration, Philadelphia, Pa. July 1966.

This article is based on a paper given at the 22nd Annual Purdue Industrial Waste Conference, May 2-4, 1967.

OUTLOOK

OWRR Covers the Waterfront

With no special mission-oriented responsibility and no in-house research, the Office of Water Resources Research fills a unique niche among the many federal agencies supporting water resources research

"The U. S. had no continuing, comprehensive, systematic water research program until the Office of Water Resources Research was created in mid-1964. Now we are going to provide that program," says Roland R. Renne. First director of OWRR, he came to the Government after more than 20 years as president of Montana State University and as an active participant in many assignments on water resources advisory groups. Dr. Renne and his staff are now in the final stages of planning OWRR's program for fiscal 1968. The plans call for increased expenditures in all current phases of the program, plus a new venture, the Water Resources Scientific Information Center.

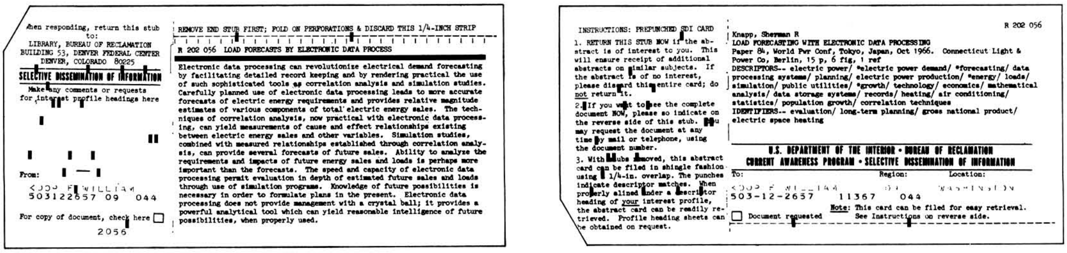
"Many government departments and agencies are active in the water field," Dr. Renne points out. "But OWRR is unique in some ways. We have no special mission-oriented responsibility, we have no in-house research. Our bailiwick is the total water picture. We are free to consider all the many uses of water—domestic, industrial, waste disposal, agriculture, recreation, natural beauty, forests, wildlife, fisheries, and transportation. Then we can try to fill in the critical gaps."

Dr. Renne also sees OWRR as a means of increasing the academic community's involvement in the water research effort: "About 100 universities are now receiving OWRR funds. As our program develops, we hope to involve at least half of the 500 or so universities in the U. S. who offer graduate work."

OWRR's research funds are handled in a number of ways. The Water Resources Research Act of 1964, which created OWRR, specified that each state and Puerto Rico should set up a water resources research institute at its land grant college or university (or some other institution if designated by the legislature). These institutes, now in existence for about two years, receive annual allotments from OWRR to carry out research programs. The act authorized $87,500 in fiscal 1967 for each institute and $100,000 in 1968. Each institute draws up its own research program (which must be approved by OWRR) and administers it.

In fiscal 1967, 397 water research projects are being financed by the allotments to the 51 institutes. OWRR and the institutes try to plan projects that will further the goals that the Federal Council for Science and Technology has laid out for the federal water resources research program. (For more on this program, see page 400.)

The second part of OWRR's program involves matching grants (on a 50-50 basis). The institutes administer these grants, although the specific projects are selected by OWRR. In fiscal 1967, OWRR received 229 proposals; it financed 71 for a total of $2 million. (The act authorized $3 million, but the full amount was not appropriated.) OWRR's budget request for FY 1968 calls for $3 million. Projects financed by



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R 202 056 LOAD FORECASTS BY ELECTRONIC DATA PROCESS

Electronic data processing can revolutionize electrical demand forecasting by facilitating detailed record keeping and by rendering practical the use of such sophisticated tools as correlation analysis and simulation studies. Carefully planned use of electronic data processing leads to more accurate forecasts of electric energy requirements and provides relative magnitude estimates of various components of total electric energy sales. The techniques of correlation analysis, now practical with electronic data processing, can yield measurements of cause and effect relationships existing between electric energy sales and other variables. Simulation studies, combined with measured relationships established through correlation analysis, can provide several forecasts of future sales. Ability to analyze the requirements and impacts of future energy sales and loads is perhaps more important than the forecasts. The speed and capacity of electronic data processing permit evaluation in depth of estimated future sales and loads through use of simulation programs. Knowledge of future possibilities is necessary in order to formulate plans in the present. Electronic data processing does not provide management with a crystal ball; it provides a powerful analytical tool which can yield reasonable intelligence of future possibilities, when properly used.

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R 202 056

Knapp, Sherman R
LOAD FORECASTING WITH ELECTRONIC DATA PROCESSING
Paper 84, World Pwr Conf, Tokyo, Japan, Oct 1966. Connecticut Light & Power Co, Berlin, 15 p, 6 fig, 1 ref
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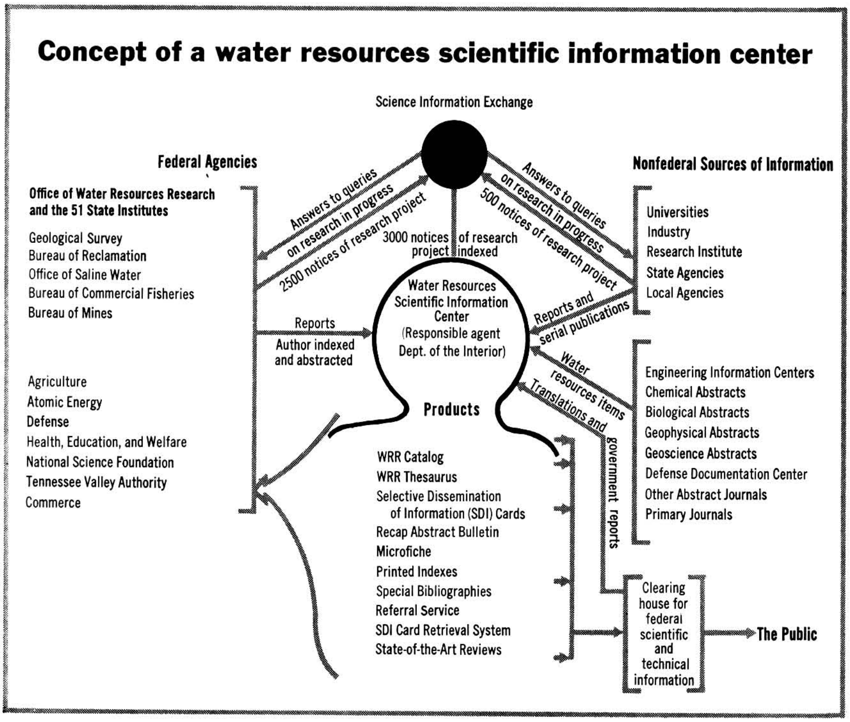

Concept of a water resources scientific information center

the allotments and matching grants are under way not only at the 51 institutes but 36 additional colleges and universities as well.

These two phases of OWRR's program serve another function—training scientists and engineers in the water resources field. In FY 1967, about 1200 students, mostly at the graduate level, received financial assistance and training as research assistants on the various projects. Another by-product of the institutes is the development of new courses of instruction, many of a multidisciplinary nature.

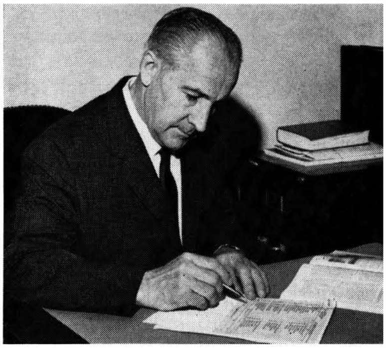
Branching out

The third part of OWRR's research program was set up by an amendment (April 1966) to the Water Resources Research Act which calls for contracts and grants open to all, with no matching fund requirement. "With this new authority," says Dr. Renne, "we will be able to tap some of the most competent research organizatons in the U. S.—universities not now in the program, as well as nonprofit and private groups. Some of these groups have talents particularly well suited to certain types of water related problems. A good example is the aerospace industries. Their experience with systems engineering and systems analysis techniques could be put to good use in water resources planning."

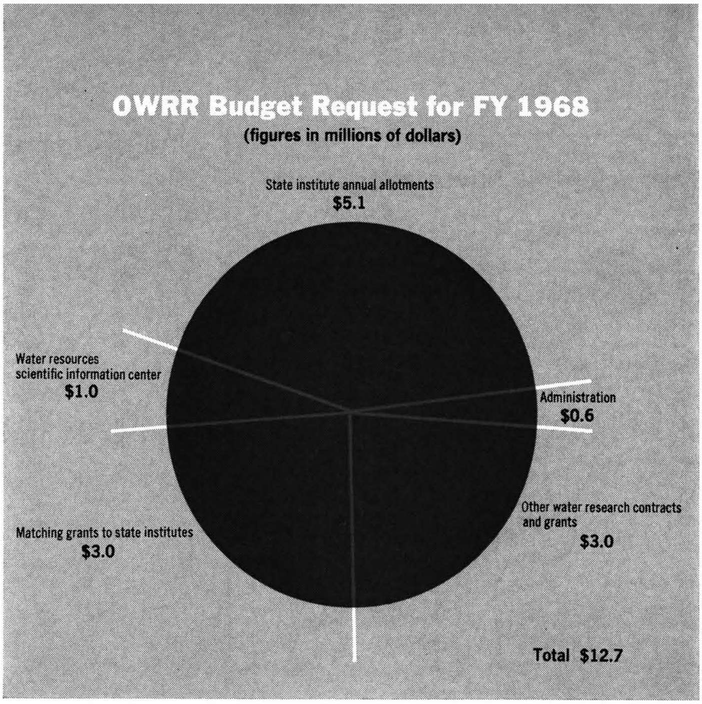
Dr. Renne is pleased with the way the research community has responded to the new program. "So far, we have received 244 proposals that would require $29 million to finance. As yet we have received no funds. The President's supplemental request for FY 1967, which just cleared Congress, included a request for $2 million for this part of the program. Congress did not appropriate the funds. We were disappointed, of course. The Vietnam buildup has tightened up funds, particularly on new projects," Dr. Renne points out. "And our program is a systematic, continuing one that includes fundamental research. But the President—and Congress, too, I believe—are behind what we are trying to do, and I'm sure we'll receive substantial support as the program develops. Both the Senate and House have approved funds for FY 1968—the Senate approving $3 million, the House $2 million."

Information dissemination

OWRR is now making plans to add a new activity to its program—the Water Resources Scientific Information Center (WRSIC). The water resources research field—in common with most other research fields—is turning out an increasing number of technical articles every year. One estimate places the number of such articles in the water field last year at about 30,000. Compounding the information problem in the water field are the many disciplines from which the investigators come. Physical scientists, biological scientists,


Roland R. Renne

No special mission-oriented responsibility



engineers, economists, planners, lawyers, and social scientists, to name just a few, can be involved in various aspects of water research.

Two ways have been suggested for dealing with the information explosion:

- A national information system encompassing all areas of science and engineering. It would be patterned after Russia's All-Union Institute of Scientific and Technical Information, an apparently successful centralization of staff, facilities, and mission. Detractors say such a system would be too large, complex, and impersonal.
- Separate information centers based on the "responsible agent concept" in which one federal agency is made responsible for collecting, evaluating, disseminating, and retrieving information in a given subject area.

WRSIC will be a test of the responsible-agent concept. It is also the first part of a long-range plan in the Interior Department for setting up a Natural Resources Scientific Information Center, according to OWRR's F. W. Koop. Other parts now envisioned in the plan include such subject areas as mineral resources and recreation. "What we learn in the WRSIC experiment—and let me stress that it is an experiment—might also be applicable to a field like agricultural research, which also involves many disciplines," according to Mr. Koop.

When WRSIC was conceived in early 1966, its job was seen as improving communication and coordination with Interior, where almost a dozen different agencies support water resources research relating to their missions. Later, the Federal Council on Science and Technology recommended that the plan be extended to all federally supported water resources research activities. (Almost 30 federal agencies now conduct mission-oriented water research.)

SDI system

In planning for WRSIC, OWRR turned to the Bureau of Reclamation, which in 1963 started a system generally similar to the concept OWRR had in mind. Reclamation uses a computer system for Selective Dissemination of Information (SDI) to 2000 of its engineers and scientists. Each month more than 800 periodicals are reviewed, along with federal and state research reports, foreign publications, and translations. Each item is indexed by keywords drawn from a Thesaurus of Descriptors. Each user is also assigned keywords which reflect his professional interests. The computer matches the keywords and provides the user with the proper SDI cards. On the average, each user gets 100 cards annually; the range is 50–300 cards.

Each card contains an abstract, the reference, and index information. If the user is interested in the material, he returns a stub on the card, indicating he wants to continue to receive similar material. At the same time he can request a copy of the full document. He can then file the abstract in a simple desk retrieval system.

WRSIC will start with this system, expanding and changing it as experience develops. The first change will be to broaden the coverage to all water resources research, not just that in which Reclamation is interested. Biology, as it relates to water resources, is a good example of a discipline that will now be covered by WRSIC, according to Mr. Koop. Another change will be to cover the foreign literature much more thoroughly. "We've had good coverage on certain types of Russian water-related project development activities. We've also covered a fair amount of European activities, but there is much more we can do there. India is good on theory, and we would expect to obtain more technical documents from that count. The point is, there are probably good ideas in a lot of places we just haven't reached in the past," Mr. Koop believes.

Under WRSIC the number of users will climb to 10,000–12,000. Most will be federal employees; outside investigators on federal grants will also be included. Not only research workers, but also planners, designers, builders, and administrators of water resource projects are encouraged to participate.

The form of the SDI card will be changed somewhat to help get a better fix on user response. "We want to know if the user is interested or disinterested in the abstract. We plan to get a printout on each user every three months, so we can see how much of what we send him he is actually interested in. If it's only a small percentage, we will have to go over his interest profile again and probably change his keywords. The ease with which we can change keywords is an advantage of the system. If a man's job changes, for example, he might need new keywords," Mr. Koop points out.

When a user wants a complete document, he will not go to WRSIC but to his technical library. If it cannot fill his request, the user—or the library—will then go to WRSIC. All material abstracted by WRSIC will be microfilmed. When a document is requested, WRSIC will send a microfiche, or a hardcopy if the user does not have microfiche equipment.

AMA Convenes Congress on Environmental Health Management

Taking a look at the environment in its broadest aspects, the American Medical Association seeks an integrated approach to the solving of environmental problems

The hazards of air pollution seem, to most people, to be roughly equivalent to the likelihood of being struck by lightning. But, as Dr. William H. Stewart, the Surgeon General of the U.S., testified at a Senate hearing last month (ES&T, April, page 271), the facts are quite otherwise. Dr. Stewart stated that there are four types of evidence which link air pollution to specific health detriment: excess mortality and morbidity during air pollution epidemics, epidemiological evidence that shows direct correspondence between incidence of disease and levels of air pollution experienced by large population groups over substantial periods of time, clinical evidence from studies of human individuals, and laboratory evidence based on animal studies.

Concerned about the incontrovertible evidence linking pollution with damage to health, members of the Department of Environmental Health of the AMA convened a congress late last month (April 24–26) in New York City to discuss environmental health management. The program allowed time for speakers from such diverse fields as architecture, economics, business, education, science, industry, government, and philosophy.

Reforming the environment

Keynote speaker R. Buckminster Fuller, Design Exploration Research Professor, Southern Illinois University (Carbondale, Ill.), opened the congress with the comments that "Man has to be seen as part of the environment, and nothing in the environment is static. The environment is an enormous complex of dynamic interpatterning of energy frequencies." Noting that churches, schools, and other agencies have already undertaken, with indifferent results, to reform man, Fuller proposed that the solution to the pollution problem lay in reforming the environment. This approach does not trespass upon the freedom of man to determine the course of his life; after all, a man can always commit suicide and remove himself from an unwanted environment, Fuller insisted.

Myriad causes of stress

If we are to achieve an environment that we are not ashamed to pass on to our children and grandchildren, we must consider such environmental problems as occupational and commuter stress, noise, vibrations, inadequate housing, poor work environments, hazards in the home, on the highways, and beneath the streets, and the social and interpersonal tensions brought upon us by better communication and transportation facilities. "In the future," said Dr. Lawrence E. Hinkle, Jr., director of the Division of Human Ecology, Cornell University Medical College (New York), "we can expect that no small part of human illness will be determined by the interaction of men with other men." In fact, Dr. Hinkle went so far as to state that there is no longer any special and limited category of diseases which should be called psychosomatic. "Either all disease is psychosomatic, or none is, depending upon how one wishes to look at it," he remarked. Dr. Hinkle listed areas in which we have made great progress, and named some concommitant ills:

- **A high standard of living and an abundant diet,** which lead to obesity and a high level of circulating fats and cholesterol in the blood. These factors lead to the accumulation of cholesterol and other lipids in the arteries which supply blood to the arteries of the heart.
- **A highly developed technology,** which has largely replaced the labor of men with the labor of machines. As a result of this inactivity, the muscles of many Americans—including the muscles of the heart—have become hypotrophic compared to the hearts of people engaged in active labor; and when a coronary occlusion occurs in a hypotrophic heart, it is more likely to cause death.
- **Rapid success in curing the major infectious diseases** of infancy and childhood, part of the reason that life expectancy of an American at birth is now approximately 70 years. Now more people are living long enough to experience the cumulative effects of abundant diet and lack of exercise.
- **An ever more elaborate society,** offering mobility and opportunity through improved methods of transportation and communication. These developments have greatly increased the requirement that people meet time deadlines, that they cope with challenges that cannot be met by direct action, that they devote themselves to long hours of purposeful activity, and that they separate themselves from the social milieus in which they originated. Such demands upon time and abilities have produced a sustained high level of alertness or arousal, which is believed to raise the level of circulating fats and cholesterol, produce frequent or sustained neural stimulation of the heart, increase heart rates over long periods, and increase susceptibility to disturbance in cardiac rhythm.
- **Wealth to adopt the habit of smoking cigarettes** in record numbers, probably because smoking makes it easier to deal with the tensions and anxieties so frequently experienced. But cigarette smoking has an adverse effect upon the blood vessels and enhances the likelihood of a coronary occlusion.

As a result of these and other stresses, heart disease, an entity which was rare 200 years ago, has become one of the most highly prevalent and lethal diseases of our time. "We can look forward to a time when the traditional environmental threats to human health and survival will have been replaced by threats of men's own making," Dr. Hinkle summarized.

The systems approach

By evolution rather than by choice, we find that our environment is dangerous to our health, and rapidly becoming more dangerous. What can be done about this situation? One solution suggested at the AMA conference was the systems approach. Dr. John A. Logan, president of Rose Polytechnic Institute (Terre Haute, Ind.), recalled that the systems approach was developed during World War II as an answer to the problems of waging war on many fronts simultaneously, and pointed out that environmental health problems involve a diversity of disciplines and might very well benefit from the same approach.

"Environmental health," he said, "involves an understanding of the multipurpose uses for which our resources may be used; it involves both area and regional planning; it involves a basic understanding of the kind of environment which we want today and which we intend to leave as a heritage for future generations to come."

A unique opportunity is ours, Dr. Logan stated, to "rectify some of the environmental insults which have resulted from past practice" and simultaneously to develop the kind of living environment for the future "which will be more nearly in keeping with our hopes and aspirations." Dr. Logan suggested that we accomplish these objectives by setting up an analysis team as recommended by the Committee on Environmental Health Problems (established on August 1, 1961, by the Surgeon General under the chairmanship of Dr. Paul M. Gross) to pursue these studies:

- Epidemiological studies of the physiologic, economic, and social effects of multiple and simultaneous low level environment exposures on the urban population.
- Consideration of environmental criteria to be used by regional and metropolitan planning groups.
- Long-range planning of environmental health research.

Dr. Logan proposed a corresponding systems team whose primary mission would be environmental health planning and establishment of environmental goals and objectives together, with alternative plans for their attainment. This team should be responsible for a continuous evaluation of the degree of attainment together with a reevaluation of goals and objectives in the light of accomplishments and failures, he said.

Another solution to environmental health problems is the more efficient use of scientific advisors in planning programs. Dr. R. Keith Cannan, chairman of the Division of Medical Sciences, National Academy of Sciences-National Research Council (Washington, D.C.), noted, in referring to advisory groups: "The common characteristic of these groups is that their members are drawn, in the main, from the community of academic science and technology. They are chosen by the executive authorities of the agencies that they serve and meet at their call. The questions that they are asked to answer are framed by the staffs of these agencies and information given to them is assembled by these staffs. An officer of the agency presides at the meetings and the minutes of the proceedings are subject to his approval.

"This method of shopping for advice is not free of bias," Dr. Cannan insisted. "The executive and the scientific formulations of a question may not be the same. Problems may take a different cast to those looking out from within than to those who peer in from without, and we all know that the way in which a question is asked may influence the response that is elicited. Executives have also been known to turn to advisory groups for the support of what has already been decided rather than to seek help in making a decision."

Dr. Cannan suggested that the solution to problems such as these lay in seeking advice from such independent sources as the National Academy of Sciences, the National Academy of Engineering, and the National Research Council.

An economic view

Economic incentives and fines might prove effective as an approach to management of environmental health. Dr. Allen V. Kneese, director of Water and Environmental Studies, Resources for the Future, Inc. (Washington, D.C.), said that the economic difficulties encountered in the fight to curb the discharge of pollutants into air and water stem from the fact that there is no market in which we can express our willingness to exchange money for smoke reduction and the like. In line with his previous statements on the economics of pollution abatement, Dr. Kneese said that he felt that a surcharge on waste effluents would be more effective than a tax incentive for the following reasons:

- The surcharge would have to be counted in the plant budget as an operating cost; then engineers who devised a cheaper way of reducing plant effluents would be rewarded for reducing operating costs.
- A tax incentive would not help the concerns which need help most. The borderline company which might have to discontinue operation if the added financial burden of pollution abatement were added should probably be given a grant of some kind rather than a tax incentive, according to Dr. Kneese.

Better communication

A fourth approach to managing environmental health was proposed by Dr. Barry Commoner, chairman of the Department of Botany and director of the Center for the Biology of Natural Systems, Washington University (St. Louis, Mo.). Education at the postgraduate level should be designed to foster better communication among the various scientific disciplines, Dr. Commoner said. "The basic knowledge of the nitrogen cycle, which could have predicted the death of Lake Erie, has, after all, been available for decades," he continued. "For about 40 years, biochemists have known that branched organic molecules tend to resist the attack of many bacterial enzymes. The importance of organic matter for aeration of the soil and for the uptake of the inorganic nutrients by plants has been known to biologists for an equally long time. Clearly, much of the available basic biological knowledge required for the prudent guidance of environmental engineering and agriculture has not been effectively transmitted to the practitioners of these applied sciences."

Dr. Commoner briefly described the successes of the Center for the Biology of Natural Systems. The center is a program of seminars and tutorials to acquaint students in a variety of disciplines with the problems involved in environmental management. The objective of the program has been to establish a collective communication, coupling the various basic sciences to the arena of environmental biology and health. The most important feature of the center, Dr. Commoner declares, is the "intellectual stimulation and excitement engendered by frank devotion to a mission which is challenging in its significance to science and rewarding in its relevance to human welfare."

The Continuing Tale of the Torrey Canyon

Coping with the pollution potential of a giant oil tanker run aground required all the scientific and engineering expertise Britain could muster. The massive clean-up is about over. The ecological effects will not be fully known for years. But by arousing public awareness, the Torrey Canyon *episode may help develop the technology to handle future—and possibly worse—episodes*

"At 0911 hours on Saturday 18th, March 1967, the *Torrey Canyon* was reported aground on the Seven Stones reef between the Isles of Scilly and Lands End. She was bound for Milford Haven with a cargo of 118,000 tons of Kuwait crude oil, and it is believed that she struck the reef when traveling about 17 knots."

In these stark terms, a British white paper launches its tale of the *Torrey Canyon.* The final chapter may not be known for years, but the moral is already clear: in its present state of the art, science and technology are hard-pressed to cope with a pollution problem of the proportions the *Torrey Canyon* posed. Oil spills have occurred over the years, several in the past few weeks. None approaches the *Torrey Canyon* as far as quantity is concerned. Furthermore, the potential threat of more spills is growing. An estimated 25–30 million barrels of oil cross the oceans daily. A tanker almost twice as big as the *Torrey Canyon* is already in service. With even bigger ones on the drawing boards there may yet be a bigger and worse *Torrey Canyon* disaster.

Keeping the coasts clear

With the *Torrey Canyon* aground, the overriding concern, says the white paper, was to keep the oil from the coasts. There were three ways to do this:

- Pump the oil into other vessels.
- Refloat the ship and tow her away, with as much as possible of her cargo within her. (Initially 30,000 tons had spilled into the sea.)
- Burn the oil in the ship.

The difficulty with the first course was that the *Torrey Canyon's* pumps were out of operation. Installing new generating equipment was ruled out because of the possibility of sparks igniting the oil gases under pressure. (On March 21, there was an explosion which killed the captain of a Dutch salvage team on board.) The alternative course of having a small pumping ship standing off the *Torrey Canyon* and feeding into another tanker standing off in safer waters would have been hazardous in calm conditions; the heavy swell in the area made it impracticable.

The salvors hoped to refloat the ship. Although extensively holed, she retained some buoyancy because the decks were completely sealed and the oil remaining in the tanks, being lighter than sea water, was for the most part held in position by pressure of the water below and the strength of the deck above. The salvors intended to increase this buoyancy by pumping compressed air into the tanks. On March 26, high seas and strong winds broke the ship's back, spilling another 30,000 tons of crude into the sea and ending the hope of salvage.

Burning the oil was considered from the outset, but this course was held in reserve for three reasons:

- The first two courses were clearly preferable.
- What little was known of this course of action was discouraging. A tanker which had caught fire in the Persian Gulf burned for more than two months and only a little more than half the oil cargo was consumed, leaving an obnoxious residue.
- A problem on this scale was without precedent. Tackling the problem on board, says the white paper, "would have involved a delicate piece of explosive surgery on the deck." Instead,

Aground. *The oil tanker,* Torrey Canyon, *began to split apart about a week after going aground at the southern tip of the British Isles. And the threat of oil-polluted beaches was realized*

PRESS ASSOCIATION PHOTOS

the Government felt that firing the oil on the sea was a likelier prospect. In experiments on an inland lake, 1000 tons of Kuwait crude were set on fire by sodium chlorate "bombs." All but 1% of the oil was destroyed.

On March 28, the *Torrey Canyon* was bombed to open up what remained of the cargo tanks and to burn the oil in them. Aviation fuel, napalm, and sodium chlorate devices were dropped to feed the fire. The fire had to be rekindled by subsequent strikes, but by March 30 practically all the oil in the wreck and in the immediate vicinity was destroyed, the white paper says. Unofficial estimates place the amount of oil burned at 50,000 tons.

Even if it had been possible to contain the oil remaining in the ship in or nearby the vessel, extensive pollution would have been inevitable. Some oil spilled out on impact; some seeped out later. Within a few hours of the wreck, Royal Navy ships were spraying detergent on the oil floating on the surface to emulsify and disperse it. In the days that followed, 53 ships joined in the spraying.

Other ways of dealing with oil at sea were considered. They included absorbing the oil with materials such as straw and vermiculite, which would coagulate the oil and remain on the surface; this approach was never used. Another approach was to sink the oil by coagulation with particulate matter such as fuller's earth, fly ash, sand, or cement. This approach was rejected because oil carried to the bottom of the sea might be released later. Fishing grounds are extensive in the affected areas, and carrying the oil to the sea bed might be more harmful than allowing it to move on the surface. Treating oil slicks with carbon tetrachloride or other chlorinated solvents was also considered, but toxicity would have created a worse situation.

The Government made plans to contain the oil in the neighborhood of the ship by a boom of expandable neoprene blocks. Such devices had proved successful in the calm waters of the Arabian Gulf and elsewhere, but no boom had been constructed for use on the high seas. By the time neoprene blocks were available on March 28, erecting a boom was impossible because of weather conditions. However, according to the white paper, the Government feels booms can be used to defend harbors, bays, inlets, and estuaries. A boom of neoprene blocks was erected across part of the mouth of the Fal but has proved unsatisfactory. A number of other booms of both urethane foam and polystyrene are being tested.

Oil Soaked Birds. *Oil spills from tankers and other ships are not new or uncommon. Here, an Avalon, N.J., resident examines dying seadivings ducks coated with black oil*

Oil on the coasts

Inevitably, oil reached the coasts. It began to arrive on March 25 and continued for several weeks. The principal beach cleaning method was by spraying of detergents shortly before the tide came up and by hosing the beach subsequently. Other solutions were improvised, depending on local conditions.

As of early April, 1 million gallons of 12 different detergents had been used. British Petroleum was the main supplier. Its compound is about 80% aromatic solvent (a kerosine extract) to dissolve the oil and 20% emulsifier to disperse the material in sea water.

Even when the oil is cleaned from the beaches, the problem is not necessarily over. Some of the oil, both untreated and emulsified, penetrates deeply into the treated beaches and might be brought up again by tidal action unless the top layers are plowed up to expose this oil.

Permanence of effects, both of oil and detergent, on animals and plants is not known. Dr. Clive Manwell, of the Marine Biological Association in Plymouth, points out that a study has been made of ecological effects along a mile of beach severely damaged in 1957 when the *Tampico Maru* released 2000 tons of oil after it ran aground off the Mexican coast. No detergent was used in the clean-up. There was still "considerable instability, even below low tide line," after 8 years. In the laboratory, Manwell says, the detergent used was more harmful than crude oil. It doesn't disperse through the sea but remains in surface layers, affecting, primarily, seabirds and intertidal shore life.

A research trawler of the Marine Biological Association has examined fish from around the Seven Stones reef. According to Home Secretary Roy Jenkins, fish were untainted and seemed plentiful as ever. He added that "close in shore, where shellfish might be affected, only very few crabs and shore-haunting shellfish have been found dead. This was in areas heavily polluted with oil where substantial quantities of detergent have been used. This is being kept under review by experts reporting to the Government's Chief Scientific Adviser, and local authorities have been asked to restrict such detergent operations wherever feasible."

Among wild birds, there have been "a lot of casualties." As of April 8, some 7000 oil-logged birds had been brought to the Royal Society for the Prevention of Cruelty to Animals, and many of these later died. The St. Agnes Bird Observatory (in the Scilly Isles) estimates that 40,000 seabirds died. According to the white paper, it may be necessary to move small populations of especially rare species. Also, some areas important for wild life will be protected by booms.

The white paper adds that "deep water fishing will not be affected nor will there be any health hazard through eating the fish. Detergent may affect plankton in areas which have been heavily treated, but these effects will be local and confined to surface waters. In shallow and estuarial waters, oil and detergent could affect lobsters and other shellfish; some oysters have been moved from their present bed to tanks and other grounds, and booms are being erected to protect creeks carrying oysters."

An old problem

Oil spills are not new. One of the largest occurred 2 years ago when U.S. vessel anchored off the French coast accidentally discharged 3000 gallons of fuel oil. In the past two months two small spills occurred in the York River from tankers headed for a refinery in Yorktown, Va. A 40-mile stretch of Cape Cod beaches was hit by oil in mid-April. One theory was that the oil came from a tanker that purged her fuel lines too close to shore. Another theory held that the oil came from a tanker sunk off the New Jersey shore during World War II; the metal finally rusted through and the crude oil was carried by the Gulf Stream up to the Cape.

What was new about the *Torrey Canyon* was the size of the spill—the 118,000 tons of crude dwarfed previous spills. It highlighted the need for new technology to deal with the larger spills. It will probably also lead to new regulations.

Another side

A somewhat different picture was presented in an article in *Nature* (April 29, page 448). As far as coastal marine life is concerned, say A. J. O'Sullivan and Alison J. Richardson, "the use of detergents constitutes a 'cure' worse than the 'disease' itself." On April 7, they visited Porthgwarra, a small rocky creek three miles southeast of Lands End. Oil had come ashore 8 or 9 days previously. According to O'Sullivan and Richardson, "animal life appeared to be perfectly normal and healthy."

Later in the same day, the shore area was sprayed with detergents. When the British biologists returned on April 8, they immediately saw the effects of spraying. "In the pools and hollows between the boulders on the lower shore there were many dead fish, and many dead invertebrates were found in the rock pools."

For coastal marine life, the biologists conclude, the mixture of emulsified oil and detergent is far more toxic than the oil itself. They see two reasons for this:

- The detergents themselves are toxic.
- The oil, when emulsified, becomes an actual part of the aqueous environment.

Shortly after the incident, the British Government requested a meeting of the Intergovernmental Maritime Consultative Organization. The 2-day meeting, held in London in early May, outlined for study possible courses of preventive, remedial, and legal action. However, it could be several years before international laws are changed because of the *Torrey Canyon.*

QUOTE...

WE ENTER THE AGE OF ENVIRONMENTAL QUALITY

In the past four years, NASA and Interior have been working closely on the definition of experiments to be performed in space for the express purpose of exploring and understanding our own planet. Herein lies the hopeful prospect of improving the human condition all over our globe. For no matter how far out we get or how exciting the discoveries, in the last analysis it is people to whom we must relate our major efforts at innovation. Our satellite program is beginning to reflect this ultimate concern for the problems of people and their immediate environmental and resource needs.

We have succeeded in opening wide the door to outer space, and now we are turning around and looking back. We have made our Earth not just the springboard to space research, but the *object* of it.

This is "the new view of the universe." This is enlightened man, using his inventive genius not as an assertion of power but as an act of faith—an acceptance of responsibility. The view from space thus becomes *not* a covetous assessment of earth from a lofty throne of power. Instead, it is an inquisitive, anxious, loving look at the planet we call home.

What intrigues me and my Department about this adventure and all the technology that goes with it is the perspective it provides in looking back on our home planet. It is in this area—the exploration of our own environment—that I see the greatest immediate rewards to our citizens for their continued, unstinting support of our space program.

One age leads to another with increasing speed. In 1945 we entered the Atomic Age. In 1957 we expanded into the Space Age. The tremendous block of conservation legislation enacted by the Johnson Administration has today placed us in yet another period which I like to call the Age of Environmental Quality. Each additional new dimension is backed up by the discoveries that came before, so that as we enter the Age of Environmental Quality, we have at our technological fingertips the tools provided by the Atomic and Space Ages. It makes a good deal of sense that the Space and Environmental Quality Ages are overlapping, for they can be used to complement each other in striking ways.

Ecological planning requires the longest look we can manage. Now, at long last, we have the equipment actually to *see* what we have grasped mentally for some time—namely, the "oneness" of our total environment. The crying need is for faster and better means of survey, and in looking for it we cannot afford to stop a mere 10 miles above the Earth. Data from space are essential and these data are vital to the welfare of every human being on earth. Their collection cannot be long delayed, for the proper use planning of our environment cannot wait. Less than 3/4 of our nation is adequately mapped, and many of *these* maps are outdated.

I can add only that in the excitement of going out into space, we cannot afford to ignore the problem-ridden Earth, which beckons us back with the knowledge we have gathered from out beyond.

STEWART L. UDALL

Sectretary of the Interior at the Symposium of the American Society of Oceanography, Houston, Tex., April 6, 1967

Power Systems for Electric Vehicles

Long range R&D, needs, and goals related to the evolution of efficient power systems for electric vehicles received intensive discussion at recent symposium

HEW's National Center for Air Pollution Control (NCAPC), the Polytechnic Institute of Brooklyn, and Columbia University sponsored (April 6–8, 1967) a Symposium on Power Systems for Electric Vehicles, at Columbia. This article covers the highlights of the symposium and the personal conclusions of its chairman, Dr. Henry B. Linford of Columbia. Participants are listed at the end of the article.

Dr. Linford was assisted by symposium co-chairmen Dr. Harry P. Gregor of Polytechnic Institute of Brooklyn and Dr. Bernard J. Steigerwald of NCAPC, by Dr. John Ludwig and Mr. Anthony Sweet, both of the NCAPC, and by Miss Donna McManus, secretary of the symposium.

The transactions of the symposium are being prepared for publication. Discussion sessions will be included in the volume along with the complete papers as delivered by the participants in the symposium. Announcement that the proceedings are available will be made in the Bookshelf section of ES&T.

The Symposium on Power Systems for Electric Vehicles opened with the discussion of a system that could be a precursor of the all-electric car, the hybrid power system. As will be clearly brought out later, batteries and fuel cells available today are not capable of giving the performance that would result in an automobile that could compete with an internal combustion engine car.

Since the development of new battery systems involves a long range research and development program, it is very likely that the hybrid system discussed by Dr. Hoffman could be more easily developed with today's technology and would have the potential of reducing pollutants by one fourth to one eighth that emitted by an uncontrolled internal combustion engine.

This hybrid system would involve an internal combustion or gas turbine engine driving a generator at constant speed. The speed would be chosen so that it is at the maximum efficiency of the engine, thus cutting pollutants to a minimum. The generator would drive the traction motor and be interconnected to an oversized secondary battery so that during acceleration and on hills the extra needed power would be supplied by the battery. When the vehicle reached cruising speed or during downhill runs the extra power from the generator would be used to recharge the batteries. This vehicle would have another advantage since when it is driven into a garage or through a short tunnel it could run on battery power, reducing the load on the ventilation system.

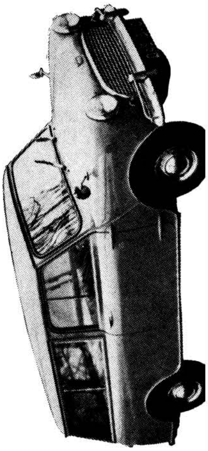
Another type of hybrid vehicle—it uses a fuel cell-battery combination in an analogous fashion to the engine-battery hybrid—is discussed in this article after batteries and fuel cells.

Types of batteries

There are two or at most three battery systems that can be considered available today for use in electric vehicles: lead-acid, silver-zinc, and nickel-cadmium. At present there are two prototype cars being run on silver-zinc batteries while the remaining prototypes are being run on the lead-acid type. The one application that may in the next few years use nickel-cadmium is the one in which

Table I. Characteristics of two electric vehicles

	Gould Electruk	A.E.I. Mini Traveller
Curb weight (pounds)	9500	2500
Battery weight, lead acid batteries (pounds)	2450	829
Payload (pounds)	3000	500
Maximum speed (miles per hour)	18	41
Range (miles)		
Multiple stops	20	—
Constant 30 m.p.h.	—	37
Four stops per mile	—	16
Battery capacity (kilowatt-hours)		
Five-hour rate	23	—
Six-hour rate	—	9.6
One-hour rate	—	6.4



Henry B. Linford
Columbia University, New York, N. Y. 10027

regenerative braking might be applied, as discussed by Dr. Wouk. The reason for this choice is that much higher charging currents may be employed when this system is used. Regenerative braking would result in large currents for fairly short periods.

Lead storage cell

Now let us take a closer look at the lead storage cell and the reasons for the limited range of cars using this power source. (See Figure 1, supplied by Dr. Barak, which shows the energy density of various systems at different rates of discharge.) Most cars built using lead-acid storage batteries have a range of about 30 miles at 30 miles per hour or at a discharge rate of 60 minutes. For this time interval, the lead-acid system has about 8 watt-hours per pound. By way of contrast, the silver-zinc system has a capacity of about 40 watt-hours per pound, the minimum energy rating that should be considered for a satisfactory automobile. Dr. Barak placed three X's in Figure 1 to indicate what might be expected from the Na/S, Zn/Air, and Li/Cl systems. Any one of these, all things being equal, would result in a car that might well have acceptable characteristics.

Range limits

Dr. Frysinger has stated the battery requirements very concisely. "For a vehicle battery, the range is limited by the energy density (kwh. per pound) of the battery, the acceleration is limited by the power density (maximum kw.) of the battery, and the off time is, of course, the time required to recharge the battery for the next discharge period."

When considering the possible range of cars using present battery technology one must take into account the driving conditions under which the battery will be used. Drs. Ferrell and Salkind show, in Figure 2, the effect of vehicle weight and acceleration loss on range. These curves show very clearly that if the vehicle cruises at a constant speed the range is much greater than when many stops are made.

Both Gould-National Batteries, Inc. and the Electric Storage Battery Co. have had experience with trucks powered by lead-acid batteries. Dr. Barak reports that there are now more than 40,000 electric vehicles—nearly all delivery trucks—licensed in England. ESB has also worked with a compact automobile powered by lead-acid batteries. Both companies report that route trucks have been successfully operated for some time now and at costs well below that for gasoline engines. Dr. Douglas also gives the operating characteristics of the Electruk and the Mini Traveller, a small car converted to lead-acid batteries by the Traction Division of A.E.I., Ltd. (Table I). The performance characteristics of the present ESB—Exide car are given by Salkind in Table II. ESB can envision that a car using present batteries might have the characteristics listed in Table II.

Silver-zinc batteries

The other battery system available now, the silver-zinc battery, has many superior electrical characteristics. Dr. Dalin estimates that about 1000 ounces of silver would be required for batteries to power a car the size of a Renault Dauphine. Dalin does not consider this to be excessive as far as capital investment is concerned since the silver can be reused time and again without end.

Dalin has compared costs of a car using the silver-zinc batteries with the use of an internal combustion engine and his figures show that the electric is a bit less expensive. However, during the discussion that followed the paper, it was brought out that the comparisons were not as close as they might be

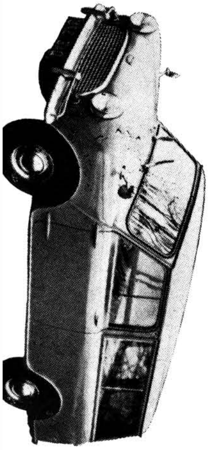
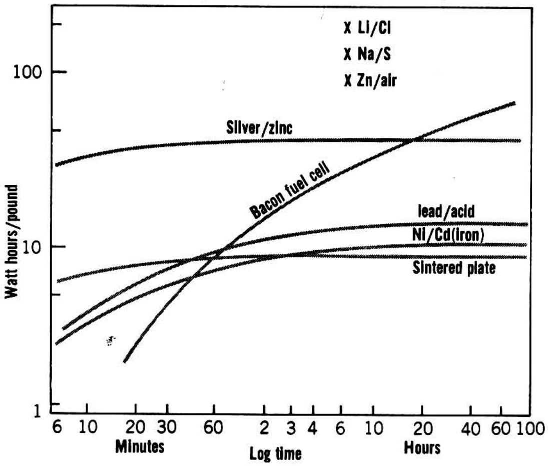
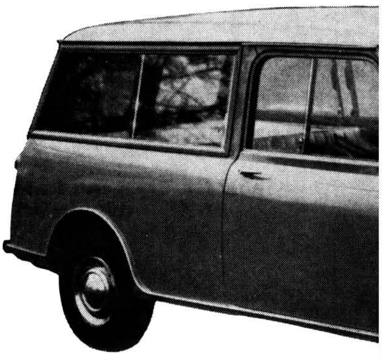


Figure 1. Most current systems cannot supply 40 watt hours per pound—a minimum requirement





The gas mileage was that of a standard-sized car rather than that of a compact the same size as the electric. Dalin's figures do show, however, that the two would be very close if a careful comparison were made.

Interesting data presented by Dalin (Figure 3) give the wattage required when the car is driven on a flat road at constant speed, the reason for the spread being wind. At 40 m.p.h. Dalin calculates that 160 watt-hours per mile are required. In city driving the range of a car equipped with four Yardney batteries each consisting of 14 85-amp.-hr. cells is close to 77 miles, depending on the speed driven and the number of stops made.

No solution yet

The conclusion one can draw from this discussion of available batteries is that it is very unlikely that cars built using these systems would be acceptable to the public. Thus, new systems will have to be considered. Dr. de Bethune discussed possible systems from the theoretical viewpoint and Dr. Gregor spoke of the possible future separators. Three batteries now in the research stage were discussed in some detail.

Dr. DeWitt presented data on the Ford sodium-sulfur experimental battery. This system, as of now in the laboratory, yields 70–80 watt-hours per pound and about the same power density or 70–80 watts per pound. DeWitt predicted that when this battery is developed a realistic figure would be 150 watt-hours per pound. The system does have a serious drawback in that it operates at an elevated temperature of 300° C. It would be necessary to keep the battery at this temperature at all times (by a self-discharge or short circuit process) or it would not prove practical. Some concern has been expressed regarding the safety of the system, but Dr. DeWitt feels that the problem of making the system safe is not a major obstacle.

Another very interesting system is the zinc-air cell. The power density of the system is 30–40 watts per pound with an energy density of 60–80 watt-hours per pound. The problems of this system have not been completely worked out in the laboratory. In order to overcome some of the difficulties of this cell very complicated systems are being used, some having the appearance of a very complicated chemical plant.

Another combination under intensive study involves lithium and chlorine. This cell should yield about 80–90 watt-hours per pound.

No doubt these possible cells will be investigated completely and will lead to at least one system of practical value in an energy storage range that would give a car with a range of 150–200 miles under either turnpike or city driving conditions.

Fuel cells

Another source of power for electric vehicles is the fuel cell. These are cells in which the reactants can be added to the cell as power is being withdrawn. As things stand, there are two operable types: the first uses hydrogen as fuel; and the second, hydrazine. Either air or oxygen can serve as the cathodes of these cells. If air is used it must be stripped of its carbon dioxide content; otherwise, carbonates build in the electrolyte when an alkaline solution is employed. Air is always available and it is not necessary to provide storage, as it is with oxygen.

The hydrazine fuel cell as developed by Monsanto Research Corp. and reported on by Mr. Dantowitz uses an air cathode. Hydrazine fuel is added to the electrolyte as the cell is working to maintain an almost constant composition of the electrolyte. He claims that as installed in an Army M-37 truck the hydrazine-air fuel cell system (excluding the motor and controller) has nearly 350 watt-hours per pound energy density when loaded for an 18-hour mission. Dantowitz believes that with a little more development effort a power unit could be built that would move a 2000-pound vehicle about five miles per pound of hydrazine. The current price of hydrazine makes the use of such a fuel cell for commercial application uneconomical. It is difficult to predict what the ultimate price would be if a large market were to be provided.

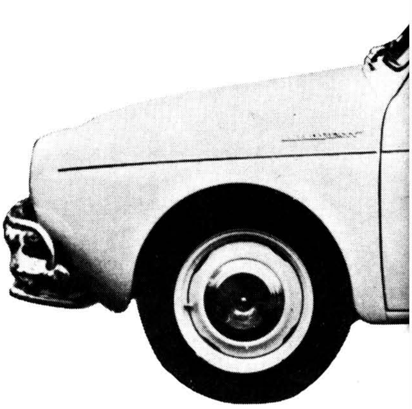
Currently the fuel cell that has many of the advantages one looks for is of the hydrogen-oxygen or hydrogen-air type. In either case the hydrogen or oxygen could be stored under pressure or cryogenically. Fuel cells using hydrogen have many advantages as mentioned by Dr. Evans, with the only product,

Table II. Comparison of performance of two electric cars

	Present ESB-Exide electric car	Projected Urbmobile using existing lead acid batteries
Maximum speed on level road	40 m.p.h.	50 m.p.h.
Range per battery charge	25–25 miles	50–60 miles
Acceleration from stop to 20 m.p.h.	3 seconds	3 seconds
Hill climbing rate (10% grade)	20 m.p.h.	30 m.p.h.

Table III. Cryogenic fuel systems are more efficient than compressed gas fuel systems

	Cryogenic	Compressed gas (at 5000 p.s.i.)	Ratio
Total volume (cu. ft.)	13	6	2.2
Total weight including vaporizers (pounds)	389	358	1.1
Total weight of product, pounds of H_2 and O_2	108	47	2.3
Total specific volume, cu. ft. per pund of H_2 and O_2	0.12	0.13	0.9
Total specific weight, pounds per pound of H_2 and O_2	3.6	7.6	0.5
Range (miles)	100–140	45–65	2.3



even theoretically possible, being water. As in the case of the hydrazine cell the costs are at present only speculative, since none of the parts is now being mass produced.

Dr. Wilcox described the General Motors Electrovan, which is powered by a cryogenic H_2–O_2 fuel cell; the H_2 and O_2 could be stored either as liquid or gas. The data in Table III show clearly that cryogenic storage is better. Table IV compares the Electrovan and the GMC van.

No intricate controls

Evans supports very strongly a hybrid system consisting of a cryogenic hydrogen fuel cell and a rechargeable battery for peak power. The hydrogen-air system makes it more suitable for trucks, buses, vans, and the like than private automobiles. The reason that this system is so attractive is that rechargeable batteries have high power densities (watts per pound) but low energy densities (watt-hours per pound). The converse is true of fuel cells, so if a hybrid system is employed the strong points of each system would be used.

Intricate controls would not be needed in such a system since a simple matching of the fuel cell and battery discharge characteristics provides proper load sharing. The fuel costs have been estimated by Evans to be of the same order as those for gasoline if increased hydrogen production resulted in a 50% decrease in the price of hydrogen, which is a very probable result. The data in Table V compare the weight of the

Figure 2. Stop-start driving decreases vehicle range

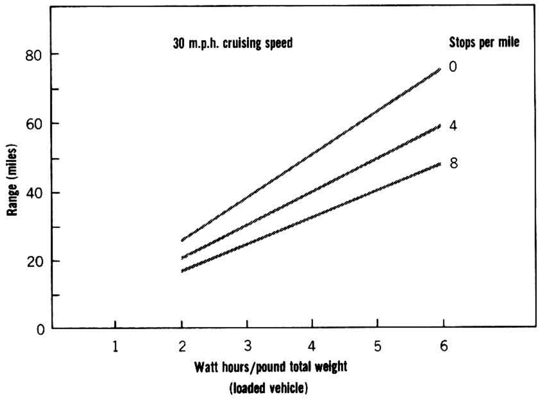
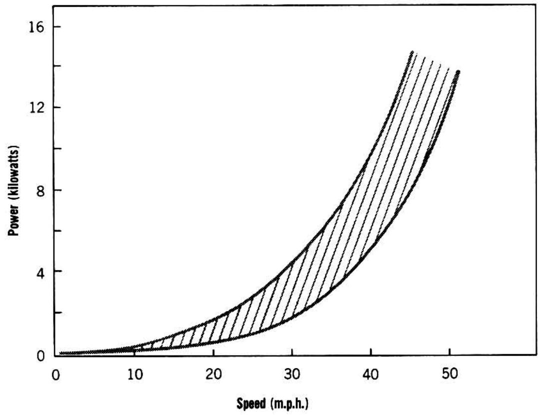


Figure 3. Power needs at each speed cover wide range



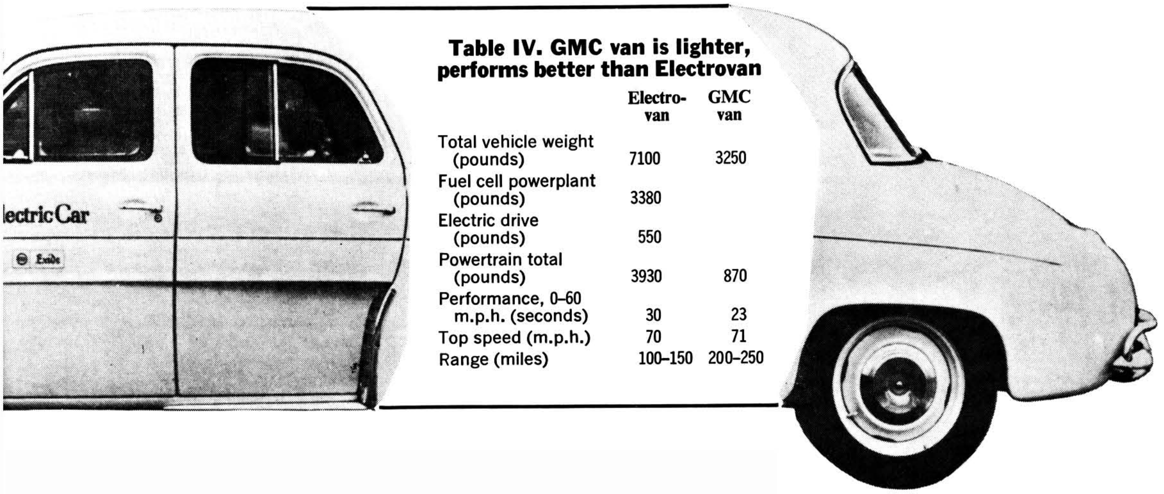
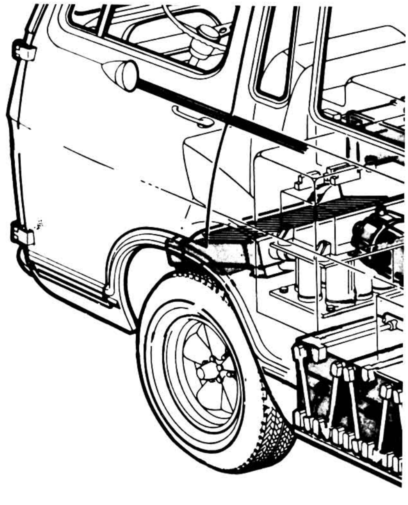


Table IV. GMC van is lighter, performs better than Electrovan

	Electro-van	GMC van
Total vehicle weight (pounds)	7100	3250
Fuel cell powerplant (pounds)	3380	
Electric drive (pounds)	550	
Powertrain total (pounds)	3930	870
Performance, 0–60 m.p.h. (seconds)	30	23
Top speed (m.p.h.)	70	71
Range (miles)	100–150	200–250



Electrovan and the proposed hybrid systems and show clearly that a reduction in the weight of the system may be obtained with no loss in performance if a hybrid system is used.

Dr. Frysinger discussed in some detail requirements for army tanks and trucks. He proposed a hybrid system using a hydrocarbon-air fuel cell. The hydrocarbon would first go through a reformer that would set the temperature of the package at 450° to 600° C. The fuel cell, battery, and reformer would constitute one very well insulated unit that would be kept hot at all times.

Another type of fuel cell in which the fuel is metallic aluminum, was discussed by Dr. Zaromb. According to Zaromb, a cell using aluminum and air is close to 26% efficient, based on the current efficiencies of aluminum utilization in the fuel cell and aluminum deposition in the electrolytic reduction process, and the operating voltages for each of these processes. As with all the other cells discussed much research and development work remains to be done on this system.

Various conference speakers have noted that it is possible at present to build an electric vehicle that will run, but that we cannot yet build one that does everything that a gasoline engine vehicle does. Due to this difference in performance as it stands now, no one would want to buy an electric vehicle, of the variety displayed on the Columbia campus during the symposium, to replace even a commuting car—unless, that is, the Government begins to intervene in the number of gasoline-driven automobiles allowed on highways during days of high smog density.

Interplay of science and politics

During the severe smog that the New York City area experienced this past Thanksgiving there was talk of excluding automobiles from the highways on just such days. In fact, since the symposium the New Jersey State Senate has passed a bill which is now being considered in the House that would grant the Governor such control.

We cannot go on as we are now. Maybe the Federal Government will have to pass a law to keep us from killing ourselves. If such a law were passed, many people would be willing to pay a little more to have a car that they could use to go back and forth to work each day, knowing full well that regardless of smog conditions they would be allowed to use the highways. We would not have anywhere near the same requirements in the purchase of that car as we would for one used to drive from Boulder Dam to Las Vegas, Nev., where the probability of being excluded from the road for "smogging up the highway" is nil.

At present there are many intangibles, but these will be multiplied when political objectives are introduced. The companies represented at the symposium should strive to make progress as quickly as possible since there are so many facets to this problem—as we discovered during the three days of the symposium.

Controls have to be improved, exotic types of batteries which will give us far better power density should be developed, and fuel cell and secondary battery systems, which at present look too much like a chemical plant, should be streamlined. The type of service needed by such systems will not be available from present-day service stations. We should let the service stations know what we are developing so that they can plan to move with us.

I believe we are going to have to deal with these problems step-wise. The development of the electric car cannot progress fast enough to take care of the short-range problem of smog.

Improvement in internal combustion engines will have to be made to ameliorate their smog forming operations. Although a discussion of the improvement of internal combustion engines was not part of this symposium, I think it is the first step to take. Even so, I am not sure that internal combustion engines can be improved to the point that the whole problem will be solved. I still think that the electric car has a place in the future, particularly as a commuting car.

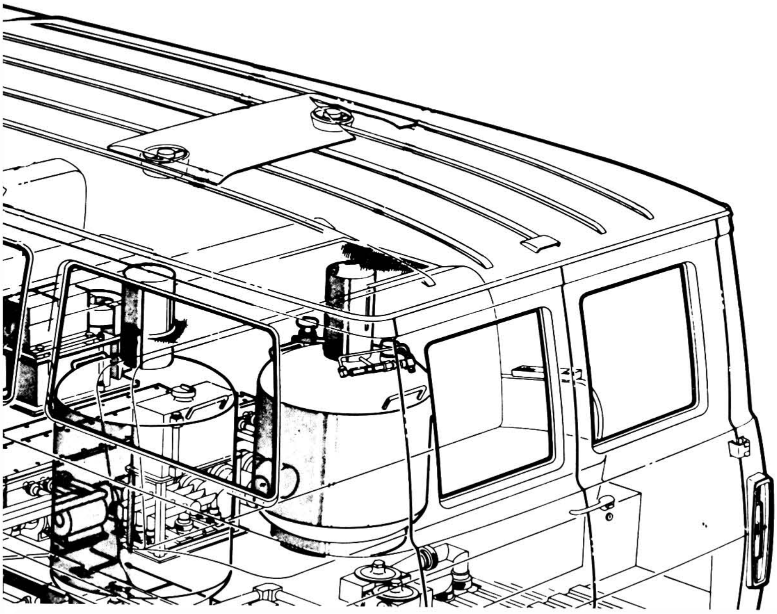


Table V. Weight breakdown for a fuel cell powerplant

	Electrovan (pounds)	Hybrid systems–this study (pounds)
Fuel cell stacks	1345	690
Peak power battery	—	427
Fluid system	1097	704
Fuel and fuel tankage	164	164
Oxygen and oxygen tankage	208	—
Electric system	569	380
Electric motor drive and controls	550	550
Power train total	3933	2915

Participants in Symposium on Power Systems for Electric Vehicles

Barak, Dr. M.
The Chloride Electrical Storage Company, Ltd.
Power Sources for Electric Vehicles

Cohn, Mr. Ernst M.
National Aeronautics & Space Administration Headquarters
NASA Work on High-Energy-Density Electrochemical Power Devices

Dalin, Dr. George A.
Yardney Electric Corporation
Performance and Economics of the Silver-Zinc Battery in Electric Vehicles

Dantowitz, Mr. Philip
Monsanto Research Corporation
A State-of-the-Art Automotive Fuel Cell

de Bethune, Professor Andre
Boston College
Electrochemical Systems

DeWitt, Dr. T. W.
Ford Motor Company
A Sodium-Sulfur Secondary Battery

Douglas, Dr. David L.
Gould-National Batteries, Inc.
Lead-Acid Batteries and Electric Vehicles

Dunning, Dr. John R.
Columbia University
Welcome Address

Eisenberg, Dr. Morris
Electrochimica Corporation
High Energy Non-Aqueous Battery Systems

Evans, Dr. George
Union Carbide Corporation
Hydrogen-Air Fuel Cells for Vehicle Propulsion

Frysinger, Dr. Galen R.
U. S. Army Electronics Command
Fuel Cell-Battery Power Sources for Electric Cars

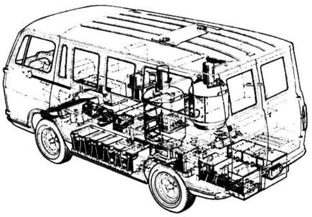
Gillis, Dr. E.
U. S. Army Engineer Research & Development Laboratories
Power Systems for Electric Vehicles

Gregor, Professor H. P.
Polytechnic Institute of Brooklyn
Separator Systems

Heath, Dr. C. E.
Esso Research and Engineering Company
Direct Hydrocarbon and Methanol-Air Fuel Cells

Heller, Commissioner Austin N.
New York City Department of Air Pollution Control
Luncheon Speaker

Helly, Dr. Walter
Polytechnic Institute of Brooklyn
Impact of Electric Power Systems on Urban Traffic Flow



Henderson, Mr. Clark D.
Stanford Research Institute
Impact of Electric Vehicles on Urban Problems

Heredy, Dr. L. A.
Atomics International
The Atomics International Sodium-Air Cel

Hoffman, Dr. George A.
University of California
Hybrid Power Systems for Automobiles

Linford, Professor Henry B.
Columbia University
Summary

Morse, Dr. Richard S.
Sloan School of Management, M.I.T.
Luncheon Speaker

Osthoff, Dr. R. C.
General Electric Company
Potential Battery Systems in Vehicle Propulsion

Palmer, Mr. Nigel I.
Leesona Moos Laboratories
Zinc/Air Batteries for the Electric Vehicle

Ragone, Dr. D. V.
General Atomics
An Electrically Rechargeable Zinc-Air Battery for Motive Power

Salkind, Dr. A. J.
Electric Storage Battery Co.
Power Systems for Electric Vehicles

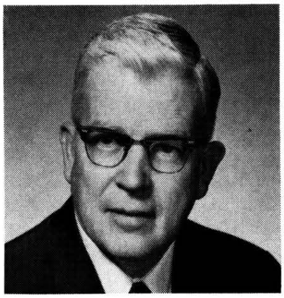
Shair, Dr. R. C.
Gulton Industries, Inc.
Lithium Nickel-Halide Batteries

Vansant, Dr. Carl A.
Operations Research Incorporated
The Mechanical Design of Electric Automobiles

Wilcox, Dr. Howard A.
General Motors Corporation
GM's Electric Vehicle Research

Wouk, Dr. Victor
Gulton Industries, Inc.
Electronic Circuits for Speed Control and Braking

Zaromb, Dr. Solomon
Zaromb Research Corporation
Aluminum Fuel Cell for Electric Vehicles



Dr. Henry B. Linford *is professor of chemical engineering at Columbia University, New York City. Previously (1937–41), he worked as a research electrochemist at the American Smelting & Refining Co. (N.J.), then joined the staff of Columbia University as an instructor in 1941, becoming assistant professor in 1946, associate professor in 1949, and professor in 1952. Dr. Linford received his B.S. (1931) at Utah State University, and his M.S. (1933) and Ph.D. (1936) in physical chemistry at Washington State University. In 1936 he was awarded the Weston Fellowship by the Electrochemical Society, and worked under the direction of Dr. Colin G. Fink at Columbia University in 1936–37. Dr. Linford is the author of numerous articles on electroplating, corrosion, and surface chemistry. He is a Fellow of the New York Academy of Sciences, and a member of ACS, Sigma Xi, Electrochemical Society, AIChE, Faraday Society, American Electroplaters' Society, and National Association of Corrosion Engineers.*

The Federal Resources Research Program

All Quality Criteria for Sulfur Oxides Set by HEW

In fiscal 1968, the Federal Government plans to pour more than $133.9 million into water resources research. In 1965 the figure was $70.0 million. There is no better index of the Nation's growing commitment to rescue—in President Johnson's words—"the clear, fresh waters that were our national heritage."

These funds come from almost 30 separate government bureaus. The task of coordinating these efforts and directing them toward long-range goals falls on the shoulders of the Committee on Water Resources Research (COWRR). Established in 1963 by the Federal Council for Science and Technology, it is now headed by Robert L. Smith. Mr. Smith is on leave from the University of Kansas, where he is chairman of the civil engineering department. In a recent interview with ES&T, Mr. Smith discussed the federal program, where it is, where it's going.

The blueprint for the program is "A Ten-Year Plan of Federal Water Resources Research," developed over a two-year period and released in February 1966. Although the report did not propose intermediate expenditure levels between 1967 and 1971, the planning target for 1968 was $143.8 million. Mr. Smith does not attach too much significance to the indicated shortfall of $10 million for the coming year: "Resolution of budgetary constraints, personnel needs, and other problems always encountered in new or expanding programs undoubtedly created some initial inertia, but it is quite obvious that agency programs are now responding to the basic objectives of the 10-year plan. The projected estimate of a $200 million program by 1971 is both reasonable and possible."

According to Mr. Smith, COWRR sees these developments which might

Federal expenditures for water resources research by category

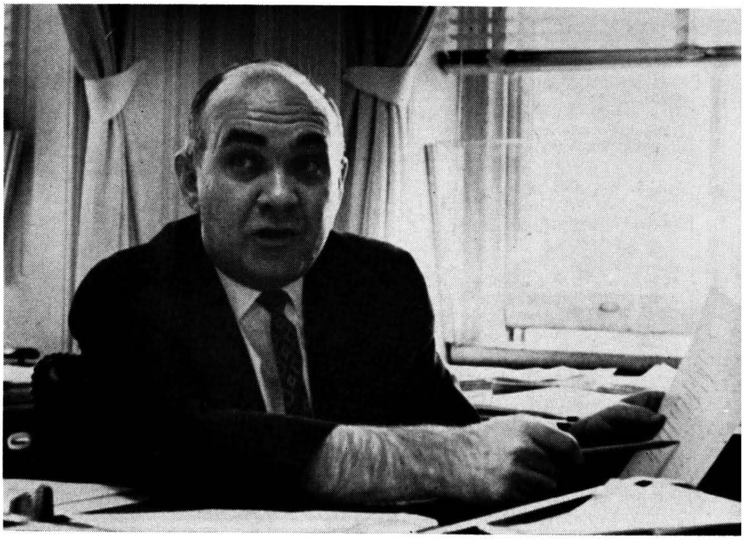
(figures are in millions of dollars; years are fiscal years)

Category	1966	1967[b] (estimate)	1968 (estimate)
Nature of water	$ 3.4	$ 1.9	$ 2.0
Water cycle	18.2	19.8	22.3
Water supply augmentation and conservation	20.2	33.8	31.1
Water quantity management and control	4.5	5.4	6.2
Water quality management and protection	22.2	25.3	45.2
Water resources planning	5.7	7.6	8.8
Resources data	2.2	1.9	2.4
Engineering works	4.8	6.3	6.7
Manpower, grants, and facilities[a]			
Education (extramural)	3.4	3.8	5.4
Education (in-house)	1.1	1.4	1.7
Research facilities	0.8	2.7	1.2
Miscellaneous	1.1	1.0	1.1
TOTAL	**87.7**	**111.1**	**133.9**

Notes: 1. Totals may not add up due to rounding.
2. Certain demonstration and development activities not included.

[a] In FY 1966, $18.0 million in grants, contracts, and research act allotments distributed in other categories; in 1967, $22.2 million; in 1968, $24.8 million.

[b] Includes OWRR supplemental appropriation of $2.0 million.



Its goal is to make water serve the needs of the people. To meet this goal, the Government will spend $133.9 million for water resources research in fiscal 1968—almost twice the amount spent just three years ago. The current thrust is on pollution control, but the remainder of the water problems are not being neglected

Federal expenditures for water resources research by agency

(figures are in millions of dollars; years are fiscal years)

Agency	1966	1967 (estimate)	1968 (estimate)
Interior Department	$59.9	$ 79.2	$100.0
Federal Water Pollution Control Administration	16.4	22.4	42.6
Office of Saline Water	21.4	30.5	26.8
Geological Survey	10.0	11.0	13.2
Office of Water Resources Research	6.0	8.5[a]	11.1
Bureau of Commercial Fisheries	2.2	2.5	2.3
Bureau of Reclamation	2.2	2.5	2.2
Bureau of Sport Fisheries and Wildlife	1.4	1.5	1.6
Bureau of Mines	0.4	0.3	0.2
Agriculture Department	17.0	18.9	19.3
Defense Department	3.9	5.7	6.6
Atomic Energy Commission	2.7	2.4	2.5
National Science Foundation	1.7	1.8	1.8
Health, Education, and Welfare Department	0.7	0.9	1.3
Tennessee Valley Authority	0.7	1.0	1.0
Commerce Department	0.7	0.8	0.8
Transportation Department	0.3	0.4	0.5
TOTAL:	**87.7**	**111.1**	**133.9**

Notes: 1. Totals may not add up due to rounding.
2. Certain demonstration and development activities of FWPCA and OSW not included
3. All FWPCA figures assigned to Interior Department.
[a] Includes supplemental appropriation of $2.0 million.

bring significant changes in the federal program:

- More widespread use of remote sensing equipment, including remote sensing from satellites, in resources surveys, and hydrologic data acquisition. COWRR is studying the National Aeronautics and Space Administration's activities for possible application to water resources management. This development will probably be implemented in the FY 1969 program.

←**Robert L. Smith**
Hamstrung by lack of data on water use

- Intensified effort on scientific and technical information. "Improvements in information retrieval and in overcoming the semantics of multidisciplinary communication are crucial to the success of water resources research efforts," Mr. Smith believes. In a related move, the Office of Water Resources Research is setting up a Water Resources Scientific Information Center (see page 386).
- Increased research on developing more efficient and accurate ways of determining the magnitude of existing water uses. During the past year, the Water Resources Council started its assessment of future U. S. needs for water. It soon found that it was hamstrung by the lack of data on how water is being used now. Current and projected research was stressing development of techniques for predicting future use. "We need," says Mr. Smith, "a well organized government-wide procedure for collecting water use data. We also need reliable information on the economic consequences of water shortages of varying kinds and degrees. And we know practically nothing on the social and economic consequences of various methods of allocating water between different geographic areas and for difference purposes. Until we develop adequate methodology and data sources, the council won't be able to develop a fully comprehensive assessment of national water needs."

Problem assessment

Another development Mr. Smith would like to see is greater use of preliminary problem assessment studies in development of research programs. These studies are particularly important, he says, in planning research on a specific problem that might have several different solutions, and, in some cases, in determining whether the true need is added research or application of existing technology.

The problem of acid-mine drainage is a good example of what Mr. Smith has in mind. He quotes the 10-year report on this problem: "Despite the importance of the acid-mine drainage problem, no survey has been made to determine what fraction of the acid comes from spoil dumps, strip mining, underground mines, and diffuse natural sources. Nor has any estimate been made of the degree of control which is required or possible. Would control of a relatively few major sources effect satisfactory control on the large rivers of

Appalachia? Must every point source, large and small, be controlled? Would control of strip mines alone solve the problem? With answers to questions such as these it would be possible to plan a research program which would attack first the areas of largest probable pay-off." (S.602, recently passed by the Senate, appears to direct the Appalachian Commission to undertake such a study, Mr. Smith says.)

Progress in research categories

In assessing progress for the year, Mr. Smith examined several of the major categories of water resources research:

Water resources planning. The 10-year plan saw this category as possibly the most promising area for both short- and long-term payout. The extramural grants portion of the program responded well, upping expenditures from $2.7 million in FY 1966 to $4.6 million in 1968. The in-house program has not significantly increased expenditures. The difficulty seems to be related to the fact that effort is fragmented among many agencies; thus, effective, coordinated paths of investigation are slow to crystallize.

Water quality management. The 10-year plan saw this category as "the number one technical problem ahead." COWRR figures reflect this, doubling between FY 1966 and 1968. The 1968 figure of $45.2 million exceeds the target for this category. The Federal Water Pollution Control Administration's research and demonstration expenditures include $18.6 million that could be added to the COWRR figures of $45.2 million FY 1968, making a total of $63.8 million. However, the Clean Waters Restoration Act of 1966 makes new demands on this research area, so the initial program targets are being revised upward.

Relative increases will probably be greatest in certain areas of the category—identification of pollutants, sources and fate of pollution, and effects of pollution.

Water cycle. Though knowledge of the water cycle is the foundation on which all water management rests, the research effort in this category is not expanding as rapidly as it should. Research in this area is not as glamorous as some of the other research efforts. Moreover, it often requires relatively long-term field observations. This combination appears to have a retarding effect, within the context of overall budgetary constraints, on both agency and public recognition of the relative importance of work in this category.

The Numbers Game

Arriving at a figure for total federal expenditures for water resources research can get hung up on definitions—principally on what should be included in the water resources category and on where to draw the line between research on the one hand and development or demonstration on the other hand. COWRR's figures take a narrow view; a broader view would add the following:

	FY 1966	FY 1967 (estimate) (millions of dollars)	FY 1968 (estimate)
FWPCA demonstration grants	$ 20	$ 20	$ 18.6
Office of Saline Water expenditure for Metropolitan Water District of Southern California's nuclear-energy desalination plant			8.0
Bureau of Reclamation weather modification program	3.0	3.8	5.0
COWRR total	87.7	111.1	133.9
TOTAL	**$ 110.7**	**134.9**	**165.5**

Extramural expenditures in Federal Water Resources Research program

The federal water resources research program is carried out by three major mechanisms:

- *In-house research performed by federal employees and aimed directly at mission-oriented problems of the agency.*
- *Extramural contracts with universities, research institutes, and industrial organizations. Again, research is oriented to mission requirements.*
- *Extramural grants to universities, research institutes, and industrial organizations. Research, in general, is unsolicited and not directed to mission requirements.*

Extramural expenditures by agency

(figures are in millions of dollars; years are fiscal years)

	1966	1967 (estimate)	1968 (estimate)
Interior Department	$34.5	$44.6	$53.6
Agriculture Department	2.7	2.8	3.3
Defense Department	0.7	1.4	1.9
National Science Foundation	1.7	1.8	1.8
Health, Education, and Welfare Department	0.2	0.4	0.5
TOTAL	**39.6**	**51.0**	**61.2**

Notes:
1. Totals may not add up due to rounding.
2. Commerce Department showed expenditures of $12,000 in FY 1966; $17,000 in 1967; $30,000 in 1968.
3. Tennessee Valley Authority showed expenditures of $1000 in FY 1966; $10,000 in 1967; $33,000 in 1968.

The activities of the International Hydrological Decade will contribute materially to the long-range goals in this research category, as well as plug some gaps in the present research program. Close to $1.4 million of the proposed budget for IHD activities in FY 1968 are included in COWRR figures for this research category.

Water supply augmentation and conservation. More than three quarters of expenditures in this research category are for saline water conversion efforts. Funds for FY 1968 dropped because the Office of Saline Water is shifting more to project development activities, which COWRR does not include in its figures. For example, $8 million requested for engineering development of the Metropolitan Water District of Southern California's proposed dual purpose nuclear energy-desalination plant is not included. Neither is the Bureau of Reclamation's precipitation enhancement program. Although this program is aimed at water supply augmentation, most of the research so far has been of a meteorological nature.

Two phases in the water conservation category are receiving practically no attention at all—conservation in domestic use and conservation in industry. One reason is that no agency has been given primary responsibility in these areas. COWRR looks for some progress in the industrial use category as a by-product of FWPCA's newly launched program in industrial pollution control. The Department of Housing and Urban Development's evolving research program is expected to consider the question of domestic use. Research in conservation in agricultural use is also expanding, an important consideration since agriculture uses such a large percentage of water.

Water quantity management and control. Research efforts continue to lag in groundwater management, owing primarily to lack of the detailed field data necessary for the complex systems encountered. During the coming year, the Geological Survey will start a program on urban hydrology. The first year's effort, principally on program design, will not be large, but this is a perplexing and urgent problem on which extensive research will be needed in the future.

Engineering works. Engineering research aimed at improving water resources development technology and at reducing development costs makes up the bulk of effort in this category. Since the research frequently is applicable to other fields, reporting of research expenditures is arbitrary. For example, the AEC Plowshare Program on peaceful application of nuclear explosives could have a potential in excavation of canals and harbors and creation of underground water reservoirs. COWRR does not include any Plowshare costs in its figures. On the other hand, Corps of Engineers studies specifically directed at evaluating the hydraulic and engineering characteristics of exploded craters are included. Expenditures on this program totaled $1.2 million in FY 1966, $2.2 million in 1967, and $2.5 million in 1968.

"Water Resources Research Catalog"
A view of the national water research effort

The scope of the national water resources research effort is spelled out in the "Water Resources Research Catalog." Prepared annually by the Office of Water Resources Research, the series presents summary descriptions of current research projects—both federally supported (inhouse as well as extramural) and non-federally supported. A comparison of the first two volumes shows the increasing activity in the field:

	July 1966	November 1964
Total projects	**3,905**	**2,046**
Federally supported projects	3,200	1,545
Non-federally supported projects	705	501
Principal investigators	2,507	1,359
Supporting agencies	160	177
Federal supporting agencies	29	21
Nonfederal supporting agencies	131	156

A small amount of the increase is due to improved reporting techniques, but most is due to increased activity. Six new federal programs were listed for the first time in the 1966 volume, including 646 projects initiated by the Office of Water Resources Research.

A wide range of organizations is listed as supporting projects, including cities, the 50 states, Puerto Rico, Canada, private industries, academic institutions, foundations, and professional societies. Topping the list is the Federal Government, with 29 agencies supporting projects:

	Number of Projects
Atomic Energy Commission	57
Department of Agriculture	598
Department of Commerce	
Bureau of Public Roads	74
Business and Defense Services Administration	1
Environmental Science Services Administration	30
Maritime Administration	3
Department of Defense	
Air Force	16
Army	52
Army Corps Engineers	123
Department of Health, Education, and Welfare (Public Health Service, Bureau of State Services, and Food and Drug Administration)	43
Department of Housing and Urban Development	3
Department of Interior	
Bonneville Power Administration	3
Bureau of Commercial Fisheries	19
Bureau of Indian Affairs	1
Bureau of Land Management	13
Bureau of Mines	8
Bureau of Reclamation	213
Bureau of Sport Fisheries and Wildlife	447
Federal Water Pollution Control Administration	331
Geological Survey	200
National Park Service	8
Office of Coal Research	2
Office of Saline Water	168
Office of Water Resources Research	646
National Aeronautics and Space Administration	14
National Science Foundation	108
Tennessee Valley Authority	28

"The sky is falling..."[1]

and the new Mettler air pollution balance measures just how much to 0.1 mg.

A modification of Mettler H analytical balances now permits the highly precise quantification of air-borne particulate matter in air pollution studies. Its wide weighing chamber and special pan accept the standard glass fiber filter webs widely used by the National Air Sampling Network.

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The new Mettler air pollution chamber and special pan can be factory-installed in any new Mettler H series analytical balance for $230 plus the price of the balance. There is an additional charge of $50 for installation on a balance already in the field.

Details of the modification are contained in Mettler Publication No. 667AP; balance specifications are contained in the new Mettler Analytical Balance Catalog. Both are available from your Mettler dealer or Mettler Instrument Corporation, 20 Nassau Street, Princeton, New Jersey 08540.

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[1] Little, C., Locky, C., Lurkey, T., et al., in English Fairy Tales, David Nutt, London, 1890.

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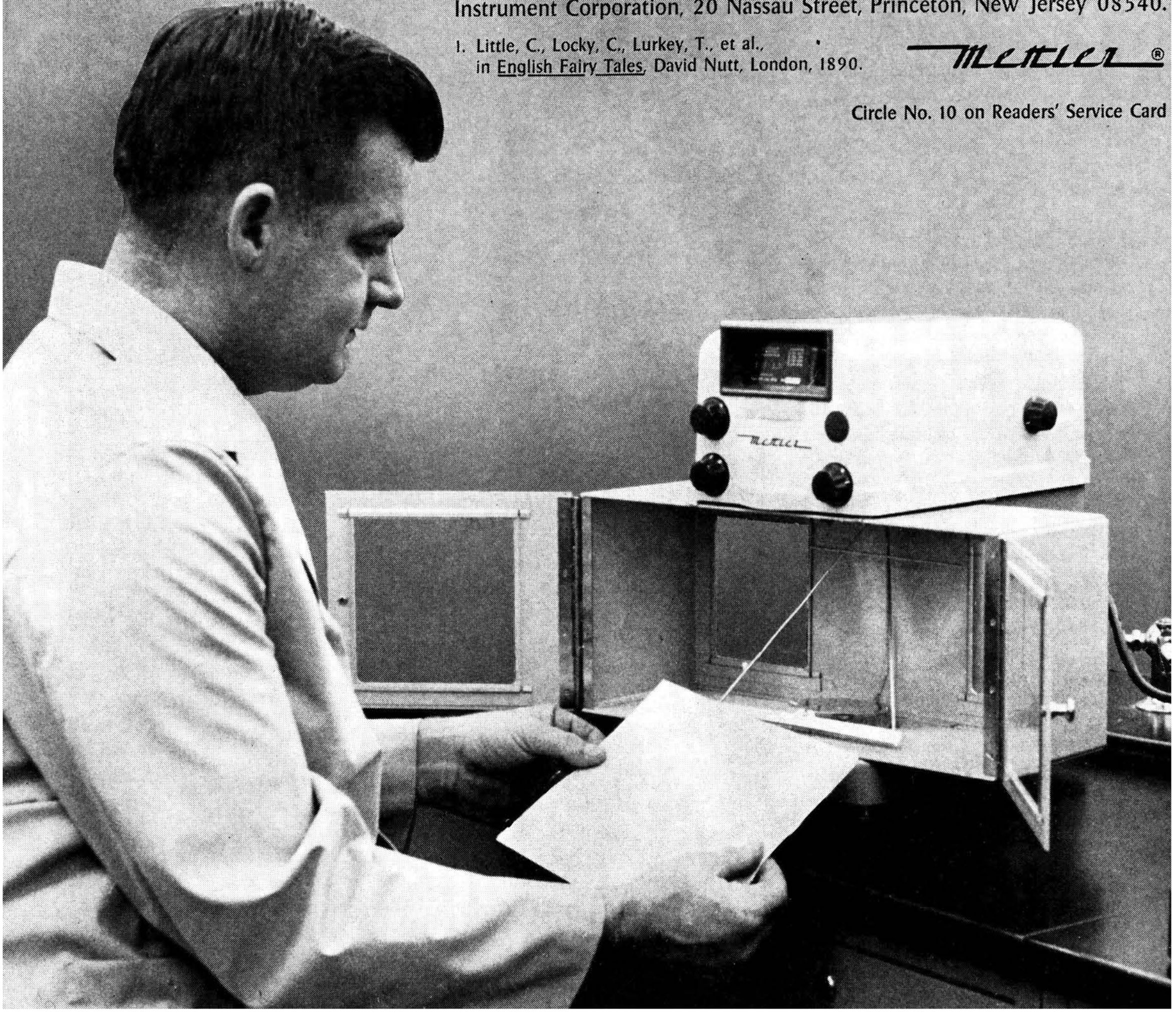

CURRENT RESEARCH

Prediction of Nitrification Effects on the Dissolved Oxygen Balance of Streams

Frank E. Stratton[1] **and Perry L. McCarty**
Department of Civil Engineering, Stanford University, Stanford, Calif.

■ A method for the prediction of the dissolved oxygen demand due to the biochemical oxidation of inorganic reduced nitrogen compounds utilizes a digital computer to estimate nitrifying rate parameters for the two-step nitrification process, including kinetic rate constants and initial concentration of nitrifying bacteria. These parameters may then be used to predict the effects of different initial nitrogen concentrations, different concentrations of nitrifying bacteria, or different temperatures on the rate of dissolved oxygen demand. The variation of rate constants with temperature is discussed and a method for evaluating the decay of viable nitrite-oxidizing bacteria in the absence of its specific substrate is presented. Examples comparing predicted and measured nitrogen changes are shown.

The process of nitrification, in which inorganic nitrogen forms are biochemically oxidized to a higher oxidation state, is of great potential significance to the dissolved oxygen (DO) balance of streams and other bodies of water. The oxygen requirement of over 4 mg. of oxygen per milligram of ammonia nitrogen oxidized to nitrate nitrogen indicates the importance of including this phenomenon in calculation of the dissolved oxygen balance, even when only small quantities of ammonia nitrogen are present.

This paper reports the development of a generally applicable method, based on the principles of biological kinetics, which permits an estimation of the concentration of viable nitrifying microorganisms, the change in concentration of inorganic nitrogen forms as a function of time, and the prediction of the theoretical rate of DO utilization due to biological nitrification.

Theory

Nitrification is a two-step process, involving first the autotrophic biochemical oxidation of the inorganic ammonia nitrogen substrate to nitrite nitrogen by *Nitrosomonas* or similar organisms. The end product of the first reaction becomes the substrate for the second oxidative process in which a different group of bacteria such as *Nitrobacter* or similar organisms oxidizes nitrite to nitrate nitrogen. In simplified form, these reactions may be written as:

$$\mathrm{NH_4^+} + {}^3/_2\,\mathrm{O_2} \xrightarrow{\textit{Nitrosomonas}} \mathrm{NO_2^-} + 2\mathrm{H^+} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{NO_2^-} + {}^1/_2\,\mathrm{O_2} \xrightarrow{\textit{Nitrobacter}} \mathrm{NO_3^-} \qquad (2)$$

Equations 1 and 2 represent the net stoichiometric changes resulting from the biochemical oxidation of each nitrogen substrate. The rate of the two oxidations, and hence the net rate of dissolved oxygen utilization by the nitrification process, is a function of the concentration and activity of the nitrifying organisms present and may be described by the kinetic parameters governing the growth and activity of biological systems.

Kinetics of Bacterial Growth

An expression for the rate of change of bacterial mass due to the combined rates of bacterial growth and organism decay has been presented by several workers (Eckenfelder and Weston, 1956; Heukelekian *et al.*, 1951) in a form similar to the following:

$$dM/dt = -a\,dC/dt - bM \qquad (3)$$

where dM/dt = rate of change of bacterial mass, mg./liter-day
dC/dt = rate of change of substrate concentration, mg./liter-day
b = organism decay parameter, day^{-1}
M = total bacterial mass, mg./liter
a = yield constant, mg. bacterial mass/mg. substrate

The term representing the rate of substrate utilization can be expressed by a kinetic equation based on the assumption that the substrate concentration, C, represents a single nutrient, the concentration of which limits the rate of bacterial activity. This form of equation is derived from the relationship first postulated by Monod (1942) to describe the rate of growth of biological organisms, and may be expressed as follows:

$$dC/dt = -kMC/(K_s + C) \qquad (4)$$

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[1] Present address, San Diego State College, San Diego, Calif. 92115

where C = substrate concentration, mg./liter
t = time, days
k = substrate utilization constant, mg./day per mg. of organisms
K_s = half velocity or saturation constant, mg./liter

For growth in a completely mixed batch culture to which substrate is added only once at time zero, the mass of viable organisms, M, increases with time and can be approximated from Equation 3 by neglecting the organism decay term, simplifying, and integrating to obtain an expression for the total mass of viable organisms as a function of the quantity of substrate oxidized:

$$M = M_o + a(C_o - C) \qquad (5)$$

Here M_o and C_o are the initial viable bacterial mass and substrate concentration, respectively, while M and C represent these values at the end of some time period, t.

Combining Equations 4 and 5 and integrating yield an equation relating time and substrate concentration as a function of kinetic parameters:

$$-\frac{1}{k}\left\{\left[\frac{-K_s}{M_o + aC_o} - \frac{1}{a}\right]\log_e[M_o + aC_o - aC] + \left[\frac{K_s}{M_o + aC_o}\right]\log_e\left[\frac{CM_o}{C_o}\right] + \left[\frac{1}{a}\right]\log_e M_o\right\} = t \qquad (6)$$

Equation 6 is a general equation which describes the decrease in bacterial substrate as a function of time for bacterial growth under conditions of completely mixed batch culture. It is similar to the equation presented by Monod (1942) to describe the growth of bacteria. Monod's equation, however, was the result of integration with bacterial mass as the variable, while the present equation results from integrating with the substrate concentration as variable. Provided that the appropriate parameters are known, Equation 6 may be used to predict the decrease in concentration of ammonia nitrogen substrate due to biochemical nitrification as a function of flow time downstream from a point of waste discharge. Here, M_o and C_o are the concentration of nitrifying organisms and ammonia nitrogen substrate at the point of discharge and M and C are these values at a distance equal to the average stream velocity times the time of flow.

Nitrite Oxidation

The concentration of nitrite nitrogen may be determined by integrating the net change in rate of nitrite production over the desired time interval, as follows:

$$C_{NO_2-N} = C_{NO_2-N,o} + \int_{t=0}^{t=t}\left\{\left[\frac{kMC}{K_s + C}\right]_{NH_3-N} - \left[\frac{kMC}{K_s + C}\right]_{NO_2-N}\right\}dt \qquad (7)$$

where subscripts NH_3-N and NO_2-N refer to the respective parameters for ammonia oxidation and nitrite oxidation.

The quantity of nitrogen used for cellular synthesis by the nitrifying organisms represents approximately 4% of the total nitrogen oxidized. (By assuming a bacterial composition of 10.9% nitrogen, averaged from a summary of bacterial formulations presented by McCarty (1964), together with the theoretical thermodynamic yield constants, discussed below, of 0.29 mg. per mg. for ammonia oxidation and 0.084 mg. per mg. for nitrite oxidation, the quantity of nitrogen incorporated in cellular mass is: $10.9\% \times [0.29 + 0.084] \approx 4\%$ of total nitrogen oxidized.) Incorporation of this source of nitrogen utilization in the above equations would slightly reduce the calculated concentrations of nitrogen forms. For simplification, however, nitrogen utilization due to biological synthesis was neglected in the above derivation by assuming complete oxidation of all of the reduced inorganic nitrogen forms.

Die-Off of Viable Nitrifying Organisms

The term representing the rate of decay of viable nitrifying organisms (bM in Equation 3) has been neglected in Equation 6, since decay is normally small when compared with the over-all rates of bacterial growth. However, under certain conditions of nitrification, as when the initial concentration of ammonia oxidizing organisms is small, there may be a considerable time lag between the introduction of ammonia nitrogen and the production of a significant quantity of nitrite nitrogen.

During this time lag, the nitrite-oxidizing organisms face existence in the absence of their specific substrate, or at best, under conditions of very low substrate at which their rate of growth is minimal. A portion of this viable nitrite-oxidizing bacterial mass would certainly decay in this unsuitable environment, the decay rate being a complex function of temperature, growth media, and other environmental conditions. Failure to include the decay of viable bacterial mass occurring under such conditions would result in the calculation of a higher than actual rate of nitrite oxidation.

The mass of viable organisms, M, at any time, t, is equal to the initial mass, M_o, plus the net algebraic sum of incremental changes in mass due both to growth and decay of the viable organisms. By combining Equations 3 and 4 this can be expressed as:

$$M = M_o + \int_{t=0}^{t=t}\left[\frac{aKMC}{K_s + C} - bM\right]dt \qquad (8)$$

Since C is itself a complex function of time, this equation cannot be solved analytically, but can be readily solved by the use of numerical techniques as discussed below.

Rate of Oxygen Consumption Due to Biological Nitrification

From Equation 1, it can be shown that 3.43 parts of oxygen are required to oxidize 1 part of ammonia nitrogen to nitrite nitrogen. Similarly, from Equation 2, 1.14 parts of oxygen are required to oxidize 1 part of nitrite nitrogen to nitrate nitrogen. The rate of dissolved oxygen utilization due to inorganic nitrification may therefore be expressed as:

$$\frac{d(O_2)}{dt} = 3.43\left[\frac{kMC}{K_s + C}\right]_{NH_3-N} + 1.14\left[\frac{kMC}{K_s + C}\right]_{NO_2-N} \qquad (9)$$

As before, subscripts NH_3-N and NO_2-N refer to nitrification rate parameters for ammonia oxidation and nitrite oxidation, respectively, and parameters M and C for each oxidation step are complex functions of time, as given above.

Prediction of Course of Nitrification

Once the respective parameters and initial concentrations of ammonia and nitrite nitrogen are known, it is theoretically possible to predict the complete course of nitrification by combining and suitably integrating the equations describing each step of the process. A digital computer program was readily written to perform the necessary steps as follows:

The time required to decrease the initial concentration of ammonia nitrogen by a small finite quantity was first calculated, using Equation 6. This time increment was then utilized to calculate the incremental change in concentration of nitrite oxidizing organisms (Equation 8), the incremental change in nitrite nitrogen concentration (Equation 7), and the theoretical rate of dissolved oxygen uptake due to the nitrification process (Equation 9). Stepwise repetition of this process by the computer provided a complete prediction of the course of nitrification and the rate of DO utilization as functions of time.

Evaluation of Rate Parameters for Nitrification Process

When we neglect the organism decay parameter, *b*, discussed below and the initial concentrations of nitrite and ammonia nitrogen present in the stream water, an examination of Equations 6, 7, and 8 indicates that there are eight remaining unknown parameters necessary to describe the complete two-step nitrification process. These parameters are:

$$\left.\begin{array}{l} a \\ k \\ K_s \\ M_o \end{array}\right\} NH_3\text{-N} \qquad\qquad \left.\begin{array}{l} a \\ k \\ K_s \\ M_o \end{array}\right\} NO_2\text{-N}$$

The yield constants, $(a)_{NH_3-N}$ and $(a)_{NO_2-N}$, may be estimated from theoretical considerations on the thermodynamics of growth (McCarty, 1964). The magnitude of the constants calculated in this manner are 0.29 mg. per mg. for ammonia oxidation and 0.084 mg. per mg. for nitrite oxidation. These theoretical yield constants are generally greater than those which can be calculated from values of substrate utilization and cell yields reported in the literature. However, the majority of the latter values are based on old cultures which would give lower than actual yield constants because of organism decay (McCarty, 1964). For this reason, the calculated theoretical values noted above have been used in this study.

The rate parameters, k and K_s, for ammonia and nitrite nitrogen oxidation are functions of environmental conditions, such as temperature, pH, and chemical composition of water in which nitrification occurs, as well as of the specific strain of nitrifying organisms present. In contrast, the concentration of viable nitrifying organisms is a function of the immediate history of the water in the reach of stream considered. If active nitrification is in progress or has just been completed in the stream or estuary water under study, or if the stream is receiving a discharge from a highly nitrifying waste treatment plant, a relatively large number of nitrifying organisms will be present in the water. If little nitrification has occurred prior to the study, very few nitrifying organisms will be present to initiate the nitrification process.

Because of this dependence on environmental parameters, the physical and chemical characteristics of the water, and the concentration of nitrifying organisms present, samples from the particular stream or water body of interest must be tested in order to evaluate the correct parameters to use for that body of water. The method of determining rate parameters is as follows:

Parameters for ammonia oxidation are determined from a nitrification test on a sample of the stream water in which ammonia nitrogen is added to the sample. The change in concentration of substrate nitrogen, as measured at various time intervals, is used in conjunction with Equation 6 to determine the best least squares fit of rate constants and initial concentration of nitrifying bacteria which describe the observed substrate decrease.

The nonlinearity of Equation 6 complicates an otherwise simple simultaneous solution. However, in this study much work was alleviated by use of a computer program which allowed estimation of these parameters through use of an algorithm developed by Marquardt (1963) and permitted a rapid solution using assumed initial starting values to speed convergence on the best-fit parameters.

Parameters for nitrite oxidation are determined in a similar manner by adding nitrite nitrogen to a water sample, observing the course of nitrite oxidation, and determining the best-fit rate parameters as described above.

This method of rate parameter determination negates the importance of the magnitude of the yield constant, so long as the same value of yield constant is used throughout all phases of the study. While the choice of yield constant does affect the magnitude of both the calculated substrate utilization constant, k, and the calculated initial concentration of nitrifying bacteria, M_o, the products kM_o and ka will remain constant, and hence any predicted nitrogen concentrations obtained by using these parameters will be the same, regardless of the initial choice of a.

The method of determining rate parameters for the nitrification process is similar to the method developed independently by Knowles *et al.* (1965) for studies on the kinetics of nitrification. These workers employed a somewhat different procedure which used all of the measured nitrogen transformations from a single ammonia oxidation test to determine rate parameters for both ammonia oxidation and nitrite oxidation. No attempt was made at predicting the course of nitrification other than fitting curves to the observed data. However, the similarity of results reported by these workers, when compared with results obtained in the present study, is indicative of the soundness of the approach for determining rate parameters.

Effect of Temperature on Nitrification Process

Once the method was developed for evaluating rate parameters, it was used to determine the effect of various environmental conditions on the nitrification process.

The effect of temperature on nitrification was studied using three different temperatures, 15°, 20°, and 25°C., and a synthetic river water which contained Ca^{+2}, Mg^{+2}, Fe^{+2}, and phosphate buffer. Each test unit was inoculated with a replicate portion of washed, blended sludge from an actively nitrifying activated sludge unit.

Tests were run at initial substrate concentrations of about 5 and 10 mg. per liter for both ammonia and nitrite nitrogen substrates at each temperature studied. Nitrogen substrate concentration was measured at frequent intervals and the results of these measurements were evaluated with the aid of the computer program noted earlier to provide a least-squares estimate of the rate parameters for each nitrification process. Results of a typical ammonia nitrogen test are shown in Figure 1 together with the substrate oxidation curve fitted

Table I. Summary of Kinetic Parameters from Temperature Study Series

Temp., ° C.	Initial Nitrogen Concn., Mg./L.	Kinetic Parameters k, day^{-1}	K_s, mg./l.	M_o, mg./l.
		Ammonia Oxidation		
25	10.6	2.52	5.59	0.0032
	5.5	1.67	1.25	0.0043
20	10.6	1.84	4.59	0.0023
	5.5	1.68	2.59	0.0033
15	10.9	0.75	3.78	0.0056
	5.5	1.05	1.85	0.0029
		Nitrite Oxidation		
25	9.7	7.56	0.50	0.018
	5.0	6.12	0.063	0.033
20	9.6	5.41	1.77	0.024
	5.0	3.98	0.34	0.061
15	9.7	3.44	0.69	0.019
	5.0	4.36	0.76	0.022

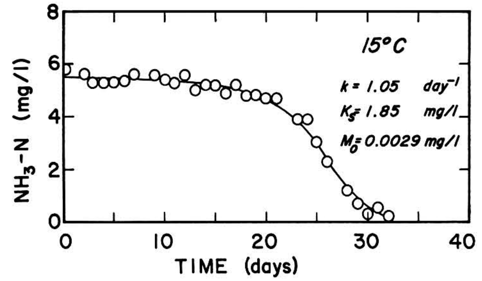

Figure 1. Oxidation of ammonia nitrogen at 15 °C., showing oxidation curve fitted to experimental data and kinetic parameters defined by this oxidation curve

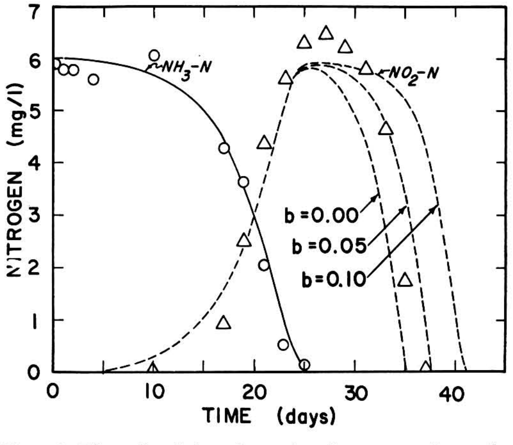

Figure 2. Effect of variation of organism decay parameter on the predicted course of nitrification

to the experimental data. Rate parameters for both nitrification studies are summarized in Table I.

The half-velocity constant, K_s, did not exhibit any marked trend with temperature or with substrate concentration. This is in contrast to the work reported by Knowles *et al.* (1965) in which the half-velocity constant was found to be temperature-dependent. Since the magnitude of the half-velocity constant is highly dependent upon the lower substrate concentrations, which are inherently most difficult to measure, it is felt that no definite conclusion can be made regarding the variation of this parameter with temperature.

The substrate utilization constant, k, however, showed a significant variation with temperature. The equations of the regression lines fitted to the values of substrate utilization constants shown in Table I are presented in Table II together with comparable data from other sources. While considerable variation exists in the magnitude of the various rates at 20 °C. —probably due to differences in physical environment and strain of nitrifying organisms—the temperature coefficients show favorable agreement for all available data. For ammonia oxidation, the rate of substrate utilization appears to increase by 7 to 9% per degree centigrade, while for nitrite oxidation, the data indicate an increase in rate of approximately 6% per degree centigrade.

The initial concentrations of nitrifying bacteria shown in Table I are in good agreement between tests within each substrate group, as would be expected, since each test was inoculated with an identical quantity of nitrifying sludge.

A statistical evaluation of confidence limits for each rate parameter would provide insight into the accuracy of the method for determining these parameters and hence of predicting the course of nitrification. Such an evaluation must await the gathering of considerably more data than are at present available. However, the coefficient of variation of the initial concentration of nitrifying organisms may be estimated from the data shown in Table I. Examination of the six initial concentrations of ammonia-oxidizing bacteria indicates a coefficient of variation of 33%, while the corresponding value for nitrite-oxidizing bacteria is 55%. It is felt that this variation is not excessive in view of the different temperatures and substrate concentrations under which the tests were performed.

Estimation of Organism Decay Parameter

The procedure for estimating the organism decay parameter, b, consisted of comparing measured nitrogen substrate values obtained during the course of oxidation of ammonia to nitrate, with predicted values, using rate parameters determined independently for the ammonia and nitrite oxidation steps. The only remaining variable under these conditions was the decay parameter, b, which was then determined by trial to obtain a best fit between experimental measurements of ammonia oxidation through nitrite to nitrate nitrogen, with the theoretically predicted course of nitrification. An example of such a trial estimation of b is shown in Figure 2.

A value of 0.05 day^{-1} (a viable mass decrease of 5% per day) was chosen from the results of several such tests as an average organism decay parameter. This value is in the normal range found by others (Eckenfelder and O'Connor, 1961) for heterotrophic growth in biological systems, and was subsequently used in the remainder of this study for predicting the course of nitrification. It is not implied that this value of decay parameter will be applicable in all cases. The rate of

Table II. Comparison of Temperature Effects on Substrate Utilization Constant

Substrate	Present Study, k, Day^{-1}	Knowles *et al.*[a] (1965), k, Day^{-1}	Garrett[a,b] (1961), k, Day^{-1}	Buswell *et al.*[a,b] (1954), k, Day^{-1}
Ammonia nitrogen	$1.47(e)^{0.084(T-20)}$	$2.54(e)^{0.095(T-20)}$	$1.30(e)^{0.091(T-20)}$	$4.14(e)^{0.073(T-20)}$
Nitrite nitrogen	$4.90(e)^{0.056(T-20)}$	$12.3(e)^{0.059(T-20)}$	...	...

[a] Corrected, to be comparable on basis of yield constants used in the present study.
[b] Calculated from data presented on growth rate and temperature.

organism decay is a function of environmental parameters and may vary widely under other conditions than those of the laboratory studies conducted herein. For accurate results, the magnitude of this parameter for other waters should be evaluated using a sample of the water under study.

Examples of Predicted Nitrogen Transformations

Two examples of predicted nitrogen transformations are shown in Figures 3 and 4. Figure 3 shows the predicted course of nitrification following the addition of 50 mg. per liter of ammonia nitrogen to a synthetic river water sample at a temperature of 25°C. under the same conditions of nitrifying activity and chemical environment used in the temperature study series. Also included in this figure are experimentally measured nitrogen substrate concentrations for a laboratory test conducted under these conditions. The course of nitrification and the rate of dissolved oxygen utilization due to the nitrification process were predicted by use of the numerical

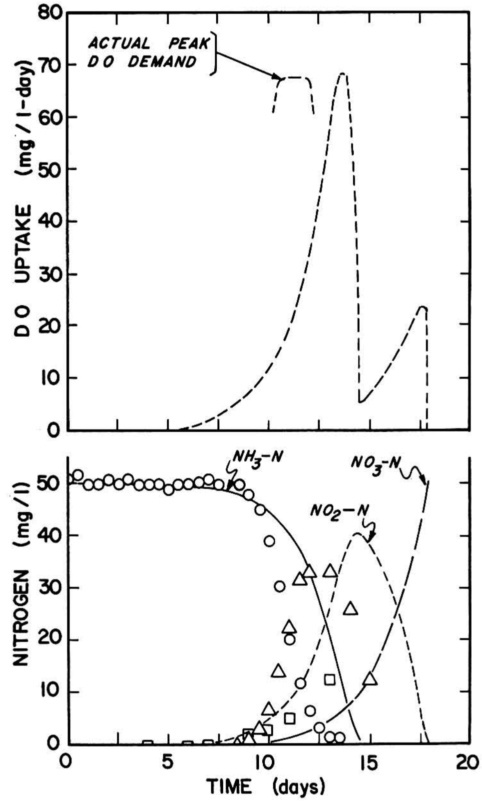

Figure 3. Predicted nitrogen transformations under conditions of nitrogen substrate concentration different from those used in temperature studies

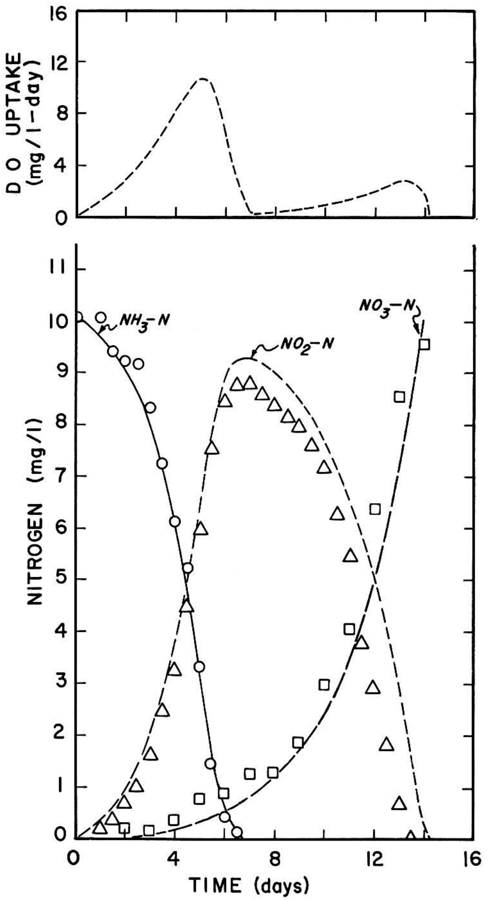

Figure 4. Predicted nitrogen transformations using modified Lewis media

integration program discussed above, in conjunction with the average rate parameters for ammonia and nitrite nitrogen oxidations determined from the 5 and 10 mg. per liter of nitrogen substrate concentration tests in the temperature study series. *The experimentally measured nitrogen substrate concentrations shown in Figure 3 are shown only for comparison with the predicted course of nitrification. None of the data shown was used in calculating the rate parameters from which the theoretical course of nitrification was predicted.*

The theoretical rate of dissolved oxygen utilization is shown above the figure of nitrogen transformations to indicate the variation of this rate with the nitrification process. The approximate location and magnitude of the actual peak DO demand were determined from the slope of the lines indicated by the experimental measurements of ammonia and nitrite, and have been plotted for comparison with the peak predicted demand.

Figure 4 shows in a similar manner the measured and predicted course of nitrification for a test conducted in conjunction with a series of tests used for rate parameter determinations in modified Lewis' media (Stratton, 1966). The concentration of nitrifying bacteria used to inoculate this sample was one half the concentration used in other tests of this series. Rate parameters used for prediction were the average of those determined for the remaining samples in the series, except for the concentration of nitrifying bacteria which was corrected by the factor of one half noted above. *Again, it should be emphasized that the experimental measurements shown in this figure are shown for comparison only and were not used for predicting the course of nitrification.* Predicted and observed values were close and the theoretical rate of DO uptake is therefore essentially identical to the predicted rate shown.

Engineering Significance

The method of evaluating kinetic parameters with the aid of a digital computer to determine the best least-squares estimate of the parameters from the results of simple nitrifying batch tests has been demonstrated to provide a rapid and reasonably accurate means of obtaining these parameters under conditions which closely approximate those found in the natural environment.

Substitution of the determined parameters into a computer program for predicting the course of nitrification then permits the prediction of the extent of nitrification and dissolved oxygen demand due to nitrification under a wide variety of conditions. The usefulness of the method herein presented lies in this ability to predict the effects of different initial nitrogen concentrations, different concentrations of nitrifying bacteria, or different temperatures on the course of nitrification.

Prediction of the rate of oxygen utilization due to oxidation of the inorganic nitrogen forms, together with the rates of oxygen utilization and replenishment due to other processes occurring, gives a complete picture of the dynamics of the oxygen cycle within a stream, and permits the calculation of the dissolved oxygen concentration at any point within the reach of stream considered. Prediction of the dissolved oxygen concentration in stream water permits adjusting waste flows into the stream water or diluting flows from upstream impoundments in order to maintain any desired minimum dissolved oxygen concentration within a given reach of the stream.

A comparison (Stratton, 1966) of nitrification rate parameters reported in the literature indicated that a wide variation in magnitude exists (up to a 300% variation in the magnitude of the substrate utilization constant calculated from reports by different workers studying ammonia oxidation at corresponding temperatures). The differences in reported rates, as well as differences observed in the present study, are probably due to differences in the many environmental factors affecting growth of the nitrifying organisms, as well as the particular strain of nitrifying organism considered. These factors point to the necessity of evaluating the nitrification rate parameters using samples of the stream water under consideration rather than attempting to choose "approximate" rate parameters from other sources.

Limitations of Method

Nitrification due to organisms attached and growing in the stream bed had not been considered in this model. The effect of such growth, if present, would be to increase the over-all rate of nitrification within the stream, the course of nitrification proceeding more rapidly than would be calculated on the basis of growth due to suspended organisms alone. Since insufficient data are available at the present time from which to draw conclusions, the possible contribution of stream bed nitrification to the over-all nitrification process in a stream must be determined by future evaluation in the field.

Conclusions

A method based on the principles of biological kinetics permits the prediction of dissolved oxygen demand due to the biological oxidation of reduced inorganic nitrogen forms in streams. The magnitude of the kinetic parameters for this model can readily be estimated under conditions closely approximating those of the natural environment by use of a digital computer to determine best-fit parameter values from the results of simple nitrifying batch tests.

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Identification of a Cholinesterase-Inhibiting Compound from an Industrial Effluent

John I. Teasley

Southeast Water Laboratory, Federal Water Pollution Control Administration,
U. S. Department of the Interior, Athens, Ga.

■ Water and hydrosoil samples were collected from the outfalls of chemical manufacturing plants, the Ashley River, and Charleston Harbor, S.C., and were analyzed for organic thiophosphate and organic chloride compounds by the use of column chromatography, gas chromatography, infrared spectroscopy, nuclear magnetic resonance spectroscopy, and mass spectroscopy. The combination of these analyses proved that *S,S,S*-tributyl phosphorotrithioate, a cholinesterase inhibitor, was present in the effluent from one of the plants. This compound was formed naturally in the waste effluent by oxidation of *S,S,S*-tributyl phosphorotrithioite, which was manufactured at this plant.

During extensive fish kills in the Charleston Harbor, S.C., area (Williams and Sova, 1966), water and hydrosoil (mud) samples were collected from the harbor, the Ashley River, a stream which flows into the harbor, and industrial effluents which were being discharged into the Ashley River. These samples were screened for the presence of organic thiophosphate and organic chloride compounds by gas chromatography, since it had been determined previously that a pesticide manufacturer was discharging untreated waste directly into the river.

Method

The water samples were extracted with chloroform (Teasley and Cox, 1963) and the extracts were concentrated in a Kuderna-Danish evaporator.

The hydrosoil samples were placed in a glass tray, air-dried at room temperature, ground, and thoroughly mixed, and a portion was taken for extraction (Teasley and Cox, 1966). The extracts were concentrated in a Kuderna-Danish evaporator. The concentrated extracts from the water and hydrosoil samples were then processed identically.

The extracts were chromatographed on activated Florisil columns (Johnson, 1962; Mills, 1959) using a mixture of 6% diethyl ether and 94% petroleum ether, followed by a mixture of 15% diethyl ether and 85% petroleum ether, and the fractions were collected separately. The ether fractions were evaporated, made to a known volume with benzene, and subjected to gas chromatography. A 4-foot, $^{1}/_{4}$-inch o.d. aluminum column packed with 5% (w./v.) DC 200 oil (12,500 centistokes) on 30- to 60-mesh acid-washed Chromosorb P was used. The gas flow was 120 cc. per minute and the column temperature was 180° C.

Microcoulometry (Coulson *et al.*, 1960), using the silver cell for halogen or the triiodide cell for sulfur, was used for the detection system. Samples which did not contain a halogen or sulfur atom were discarded.

The chromatograms of the 6% diethyl ether fractions revealed a peak by both detection cells, with an identical retention time showing the presence of a halogen and a sulfur atom in the compound producing the peak. The chromatograms of the 15% diethyl ether fractions revealed a peak by only the triiodide cell, showing the presence of sulfur in this compound.

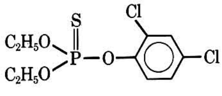
Aliquots of the 6 and 15% diethyl ether fractions in benzene containing approximately 25 μg. of each of the residues producing the gas chromatographic peaks were evaporated to apparent dryness and dissolved in diethyl ether. With a syringe, the ether solutions were transferred to powdered potassium bromide. Micropellets were pressed and infrared spectra were measured (Payne and Cox, 1966).

The benzene containing the remaining residue from the 15% diethyl ether fraction was evaporated, the residue dissolved in deuterated chloroform and transferred to a nuclear magnetic resonance tube, and a small amount of tetramethyl silane added. A nuclear magnetic resonance spectrum was measured.

The contents of the nuclear magnetic resonance tube were transferred and again evaporated. A portion of this residue was then submitted for analysis by mass spectrometry.

Results

All the samples which revealed peaks in the 6 and 15% diethyl ether fractions by gas chromatography came from the waste effluent and common drainage ditch of a chemical firm which produces *O,O*-diethyl *O*-2,4-dichlorophenyl phosphorothioate:



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and *S,S,S*-tributyl phosphorotrithioite:

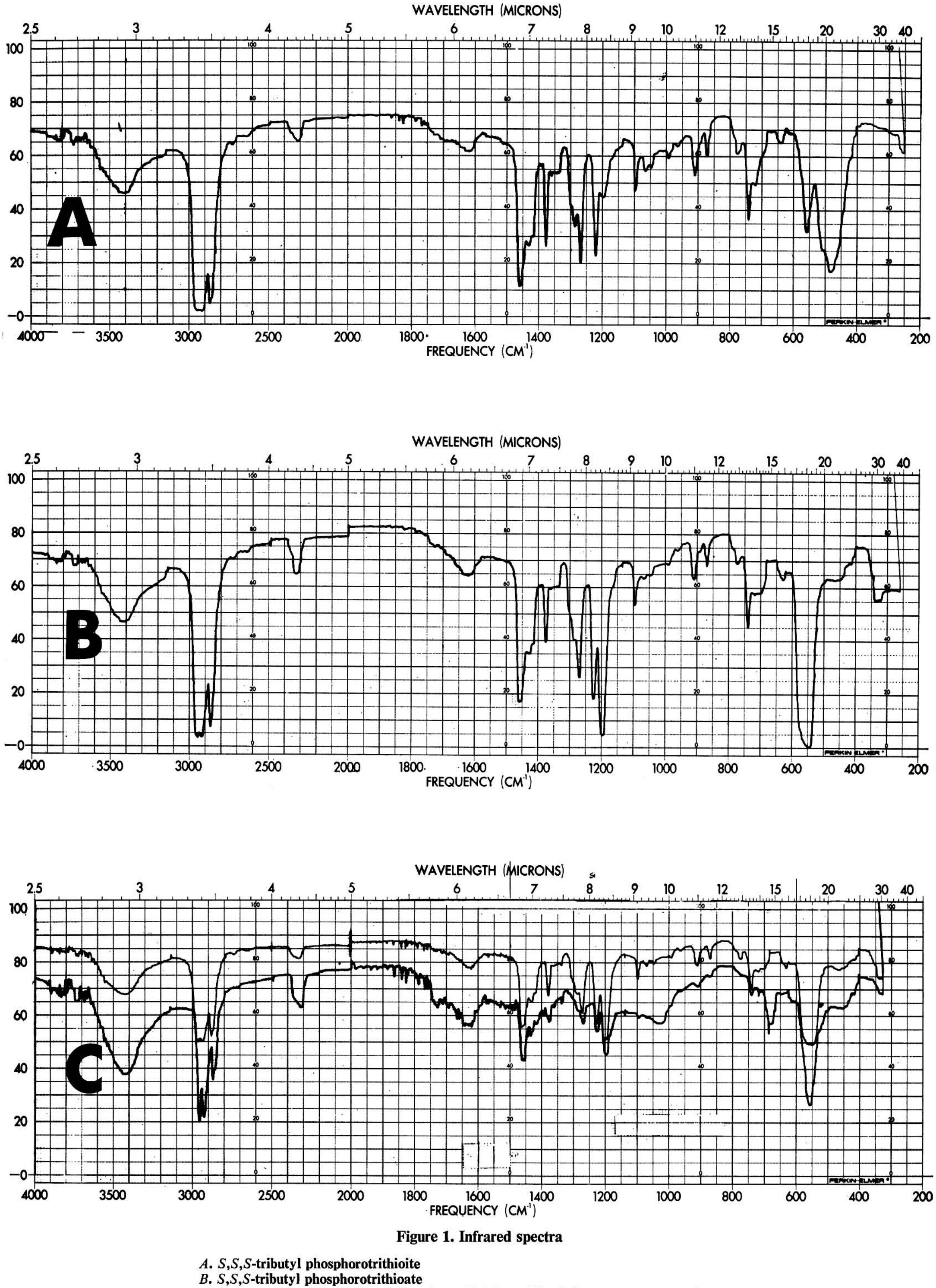


Figure 1. Infrared spectra

A. *S*,*S*,*S*-tributyl phosphorotrithioite
B. *S*,*S*,*S*-tributyl phosphorotrithioate
C. Top spectrum *S*,*S*,*S*-tributyl phosphorotrithioite oxidized, bottom spectrum unknown

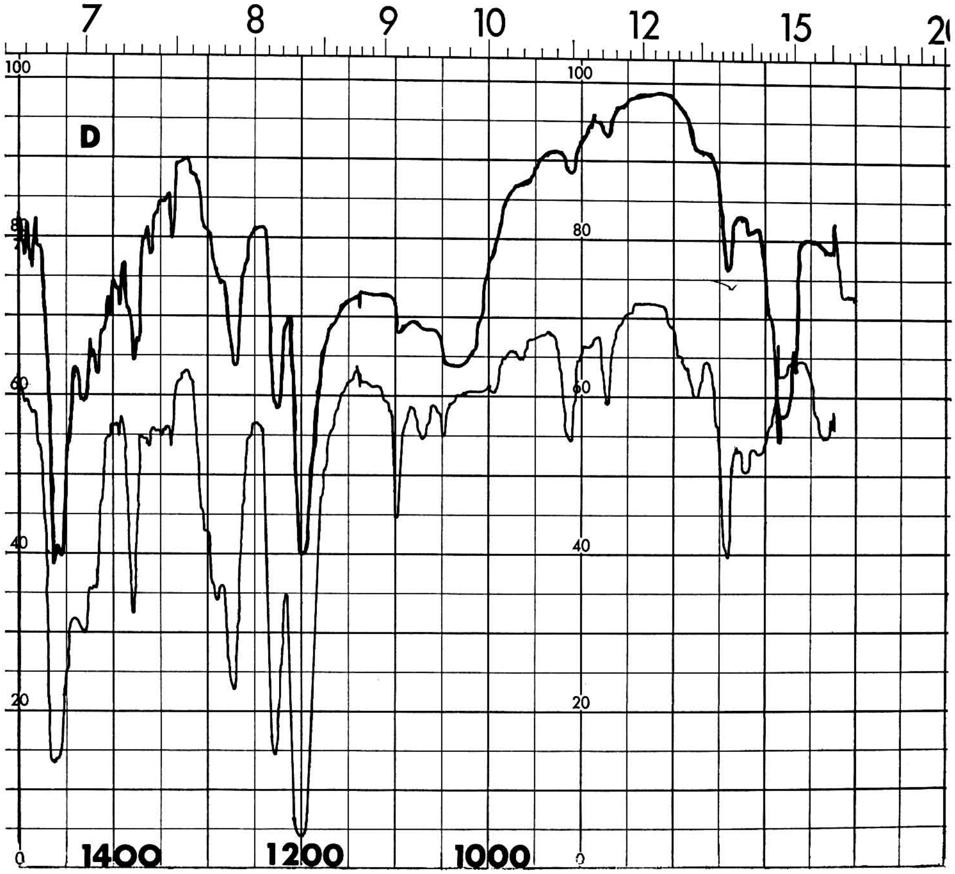
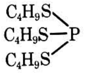


Figure 2. Infrared spectra

2× scale expansion of spectra *C* (Figure 1) from 1400 to 1000 cm.$^{-1}$



$$\begin{array}{l} C_4H_9S \\ C_4H_9S-P \\ C_4H_9S \end{array}$$

II

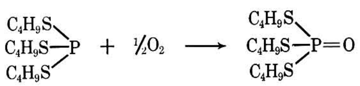
Reference standards of these two compounds were obtained and subjected to gas chromatography using both detection cells. The retention time of I was identical to that of the compound in the 6% diethyl ether fraction, eluted from Florisil in this fraction, and also responded to both detectors. The identification of the unknown compound in the 6% diethyl ether fraction as I was confirmed by infrared spectroscopy.

The unknown compound which eluted from the Florisil column in the 15% diethyl ether fraction had a longer retention time on the gas chromatographic column than II; therefore, these compounds could not be identical. The infrared spectrum (Figures 1 and 2) of this unknown compound in the 15% diethyl ether fraction and the infrared spectrum of II were similar except for a strong absorption peak at 1200 cm.$^{-1}$ in the unknown spectrum.

The nuclear magnetic resonance spectrum (Figure 3) of the unknown (*C*) and II (*A*) showed considerable differences in the definitive portions of the spectra which are the lowest field multiplets. These signals arise from the three methylene protons bonded directly to the phosphorus. In spectrum *A*, this multiplet is centered at tau (*T*) 7.2, whereas in *C* it is centered at *T* 7.0. This paramagnetic shift in *C* is due to an electronegative moiety which is absent from *A*. A further difference is noticeable in the signal pattern of the low field multiplet. In *A* there is a quartet in which one of the center peaks exhibits a further splitting. In *C* there is a distinct quintet in which all peaks are separated by the same value, 7 cycles per second.

The mass spectra (Figure 4) of the unknown (*C*) and II (*A*) show a different fragmentation pattern. The unknown has an *m/e* 314, where II has an *m/e* 298.

II is easily oxidized to *S,S,S*-tributyl phosphorotrithioate (III) (Kosolapoff, 1950) by the following reaction:



$$\begin{array}{l} C_4H_9S \\ C_4H_9S-P \\ C_4H_9S \end{array} + \tfrac{1}{2}O_2 \longrightarrow \begin{array}{l} C_4H_9S \\ C_4H_9S-P=O \\ C_4H_9S \end{array}$$

II III

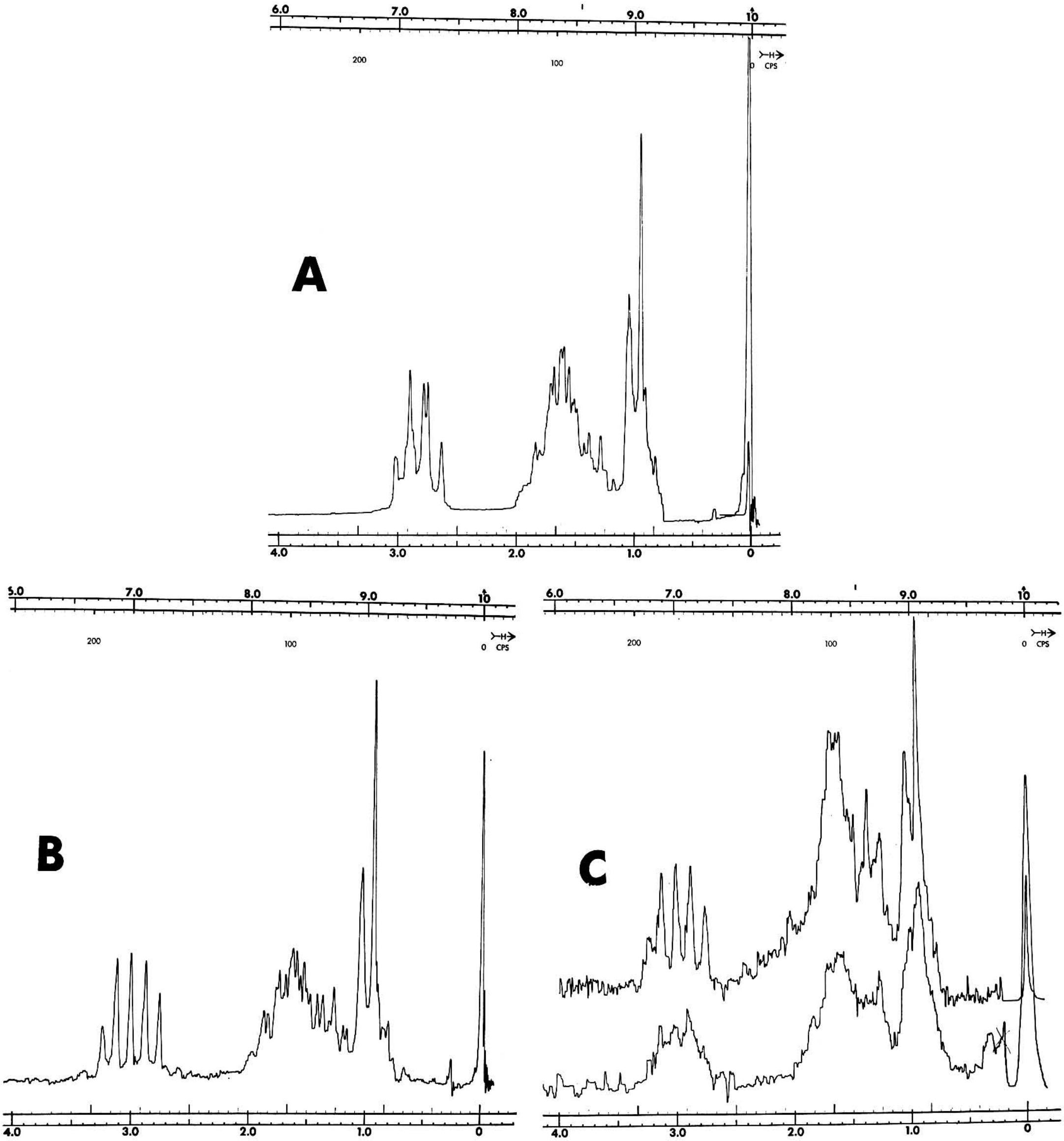


Figure 3. Nuclear magnetic resonance spectra

A. *S*,*S*,*S*-tributyl phosphorotrithioite
B. *S*,*S*,*S*-tributyl phosphorotrithioate
C. Top spectrum unknown, bottom spectrum *S*,*S*,*S*-tributyl phosphorotrithioite oxidized

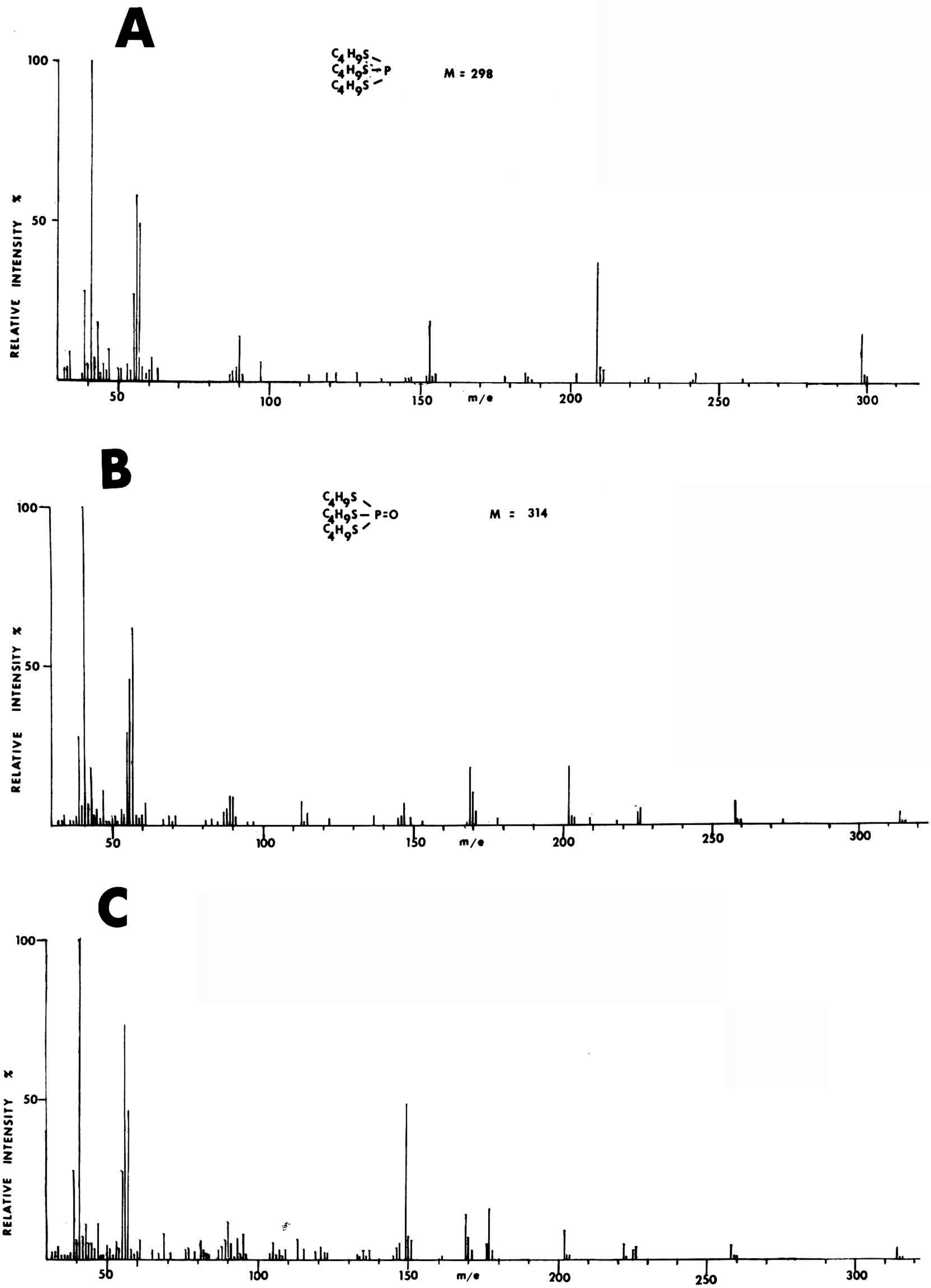


Figure 4. Mass spectra

A. *S*,*S*,*S*-tributyl phosphorotrithioite *B*. *S*,*S*,*S*-tributyl phosphorotrithioite oxidized *C*. Unknown sample

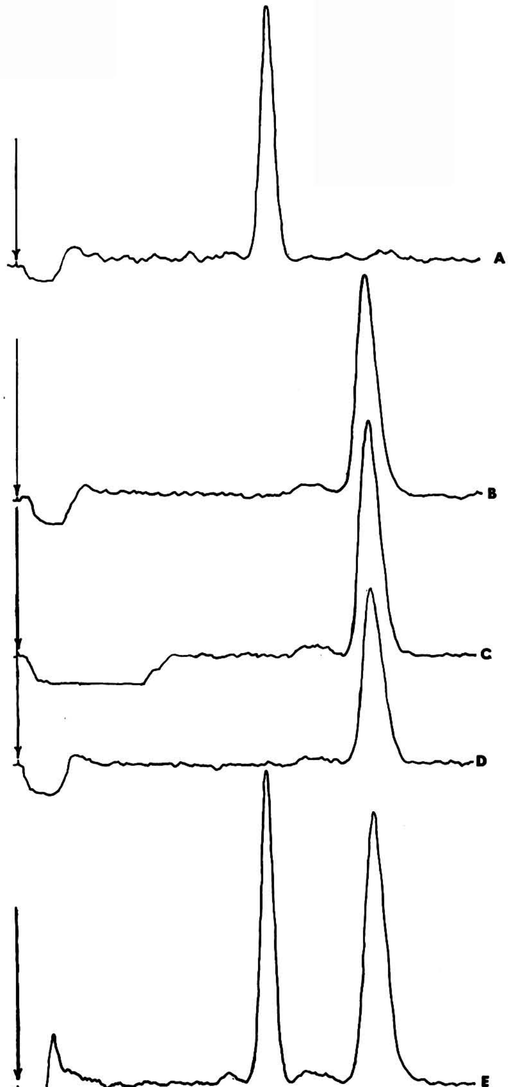


Figure 5. Microcoulometric gas chromatograms of *S,S,S*-tributyl phosphorotrithioite and *S,S,S*-tributyl phosphorotrithioate

A. 0.46 μg. of *S,S,S*-tributyl phosphorotrithioite
B. Unknown sample
C. Oxidized *S,S,S*-tributyl phosphorotrithioite
D. 0.39 μg. of *S,S,S*-tributyl phosphorotrithioate
E. 0.57 μg. of *S,S,S*-tributyl phosphorotrithioite and 0.57 μg. of *S,S,S*-tributyl phosphorotrithioate

The strong absorption peak in the infrared spectrum of the unknown compound from the 15% diethyl ether eluate at 1200 cm.$^{-1}$ is produced by vibration of the P=O linkage.

The paramagnetic shift in the nuclear magnetic resonance spectrum of the multiplet centered at *T* 7.2 to *T* centered at 7.0 is due to the presence of the electronegative oxygen.

The increase in the *m/e* value of II to that of III in the mass spectra is also caused by the addition of oxygen to the molecule.

The dilute standard of II (10 μg. per ml.) in benzene which was used for gas chromatographic retention time began to change. The fresh standard showed only one peak, but after several days two peaks could be noted, one peak with the retention time of II, the other with the retention time of III. After approximately 4 weeks the peak produced by II had completely disappeared and only the peak produced by III could be observed. Following complete oxidation in the benzene, this solution was analyzed by infrared, nuclear magnetic resonance, and mass spectrometry, giving spectra identical to that of the residue from the 15% diethyl ether fraction.

A reference standard of III was obtained from the Chemagro Corp., Kansas City, Mo., and processed in the same way as the 15% diethyl ether fraction. The gas chromatographic retention time was identical with the unknown 15% diethyl ether fraction, as were the infrared spectrum and the nuclear magnetic resonance spectrum (Figures 1, 3, and 5). (A mass spectrum was not obtained.)

Conclusions

The identity of the unknown compound in the 15% diethyl ether fraction was established as III, a cholinesterase inhibitor (Murphy, 1959) contained in the waste effluent.

Acknowledgment

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Preconcentration for Trace Analysis of Sea Waters

Timothy Joyner

Bureau of Commercial Fisheries Biological Laboratory, Seattle, Wash. 98102

M. L. Healy

Department of Oceanography, University of Washington, Seattle, Wash. 98015

Diptiman Chakravarti[1] **and Taku Koyanagi**[2]

Laboratory of Radiation Biology, University of Washington, Seattle, Wash. 98105

■ The chemical characterization of seawaters by trace-element content usually requires selective preconcentration to produce samples suitable for analysis. Phase-distribution methods which have been used for this purpose are briefly reviewed. Evaporation of the water produces a solid sufficiently concentrated for highly sensitive neutron activation techniques. Liquid-solid and liquid-liquid phase distribution provide greater concentration factors and selectivity and are used in conjunction with less sensitive methods of analysis. A simple procedure involving coprecipitation with alkaline earth salts followed by solvent extraction of transition-metal dithiocarbamates is proposed for use aboard ships at sea. With this procedure, recoveries of manganese, iron, nickel, cobalt, copper, zinc, and lead were shown to be in excess of 90%. Selective concentration of cesium and rubidium by adsorption on ammonium molybdophosphate crystals is suggested as preparation for flame emission or atomic absorption analysis.

Interest in the chemical characterization of seawaters is growing as increased attention is directed toward marine resources. As a chemical solution, sea water contains approximately 3 to 3.5% dissolved solids, primarily halides, sulfates, and carbonates of sodium, magnesium, calcium, potassium, and strontium. The concentrations of these substances vary so little that they have been classed as conservative properties of sea water. In addition to these constituents, traces of at least 50 other elements have been detected.

An analyst, faced with the determination of heterogeneities in the composition of sea waters, has two ways to approach his problem: (1) measurement of small differences at the relatively high concentrations of the major constituents, or (2) measurement of relatively large differences in the concentrations of the trace constituents. In the first case, the principal difficulty is to achieve precision sufficient to reveal differences of a magnitude several orders less than the levels of the elements being measured; in the second, the problem is to achieve analytical sensitivity sufficient for the detection of very low concentrations. Since the latter difficulty can be reduced by sample preconcentration, and wide variations in the levels of trace elements provide clear evidence of heterogeneity, trace analysis has a strong appeal to those concerned with sea-water characterization.

Methods of preconcentration for use in trace-element analysis of sea water are discussed in this report. It is our intent to examine the subject in the light of our own recent experiences in adapting these methods for spectrometric and polarographic systems of analysis, rather than to present an exhaustive review. For analysts about to tackle the trace analysis of sea water for the first time, it is our hope that the following comments and suggestions will be of help for evaluating the suitability of preconcentration methods to the analytical systems available to them. Two recent reviews (*25*, *46*) should provide excellent starting points for those wishing more complete lists of references. For those concerned with geochemical processes relating to the trace-element composition of sea water other reports (*21*, *22*, *24*, *28*, *33*, *51*) will also prove useful as a basis for further inquiry.

In seawater, the concentrations of many trace elements of current analytical interest fall within the range 10^{-11} to 10^{-8}, expressed as ratios of weight to volume (grams per milliliter). Sensitivities of analytical systems most likely to be employed for sea-water analysis are such that optimum concentrations of elements (expressed as ratios of weight to weight or weight to volume) in samples presented for analysis are on the order of 10^{-6} to 10^{-4} for emission spectrographic and x-ray fluorescence systems, 10^{-7} to 10^{-5} for molecular absorption, atomic absorption, and flame emission spectrophotometry, 10^{-7} to 10^{-4} for polarographic systems, and 10^{-10} to 10^{-5} for neutron activation methods. Polarographic (*71*) and atomic absorption (*16*) techniques have been reported for the direct analysis of several fourth-period transition metals in sea water. In these techniques, the detection limits have been lowered by about one order of magnitude below those usually claimed for commercially available instruments. The precision of the direct polarographic measurements was not given, but the direct atomic absorption measurements were reproducible to no better than 25%. Except for neutron activation, therefore, samples of sea water usually require preconcentration if the analytical system selected is to be operated within the optimum range for best precision. Even with the very great sensitivity of neutron activation analysis, it has been found useful

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[1] Present address, Life Sciences Division, Corning Glass Works, Corning, N.Y.

[2] Present address, National Institute of Radiological Sciences, Chiba, Japan.

to preconcentrate samples of sea water by removing the water and irradiating the dried salt.

In any concentration scheme for sea-water analysis, careful consideration must be given to the efficiency of recovery in the final concentrate of the elements of interest, and to the presence in the final concentrate of matter (either added as contamination during the concentration process or carried by the process from the original sample to the concentrate) which might interfere with or bias the analysis.

Removal of Water

Removal of the water permits concentration of a sample of ocean water by a factor of about 30, and therefore will provide a concentrate with many trace elements at levels sufficient for activation analysis. Water may be removed by either evaporation of the liquid or sublimation of the solid.

The advantages of sublimation, described by Schutz and Turekian *(48)*, who employed freeze-drying to prepare samples for activation analysis, are freedom from spattering, from possible volatilization of certain trace constituents, and from fractional crystallization which produces an inhomogeneous residue. One drawback to this technique is that large amounts of sodium and chlorine are present in the concentrate. Irradiation of these elements produces radioactive Na^{24} and S^{35}, necessitating a long cooling period and radiochemical separation before analysis.

For multistage concentration, water removal can be of considerable value as the first step in the preparation of samples of sea water for spectrographic, spectrophotometric, and polarographic analyses. To determine iron, Lewis and Goldberg *(38)* evaporated sea water and ashed the salty residues with perchloric acid. Iron was then extracted into a solvent for spectrophotometric measurement. All the iron in the original sample was retained in the first stage concentrate, then converted to a water-soluble form for the solvent-extraction step.

Cocrystallization

A remarkably elegant system of preconcentration of sea water for trace analysis was developed by Weiss and his coworkers *(36, 64–69)* at the U.S. Naval Radiological Defense Laboratory, San Francisco, Calif. The process, named cocrystallization, is distinguished from the more familiar process of coprecipitation by the direct crystallization, from

Table I. Cocrystallization of Trace Elements from Aqueous Solutions with Organic Reagents

(From Weiss and coworkers)

Reagent	Elements Cocrystallized	% Trace Elements Recovered				Ref.
		From lab. solution	At pH	From sea water	At pH	
α-Benzoinoxime	Mo	99–100	1.8–5.5	99	2	*(67)*
1-Nitroso-2-naphthol	Co	100	1–9	99	8[a]	*(69)*
	U	>95	7	99	7–8	*(68)*
	Fe	99	2–9			*(68)*
	Ce,Zn	>95	7			*(68)*
	Zr	97	5			*(68)*
Thionalide	Ag	100	3.5–7	92	3.5	*(36)*
	In,Hg	98–100	3.5–7			*(36)*
	Au	98	0.7			*(36)*
	Os	100	7			*(36)*
	Ta	98	3.5			*(36)*
2-Mercaptobenzimidazole	Au	99	1	99	1	*(65)*
	Sn	100	5			*(65)*
	Hg,Ag	99	1–5			*(65)*
	Ta	95– 98	1–5			*(65)*
Potassium rhodizonate	Ba	100	5–7	99	7–8[b]	*(64)*
	Pu			100	7–8[b]	*(64)*
	Ra,Sr	100	5–7			*(64)*
Ammonium dipicrylaminate	Cs	≥98	2–5			*(66)*
	Rb	≥95	2–8			*(66)*

[a] Untreated sea water.

[b] 2 volumes of 1.6% K-rhodizonate in distilled water + 1 volume of seawater.

Table II. Solvent-Extraction Systems of Proved or Possible Use for Concentrating Trace Elements from Sea Water

Elements Analyzed	Original Sample	Sequestering Agents	Solvent	Method of Analysis	Ref.
Ce	Biol. matter Sea water	Bis(2-ethyl hexyl)-hydrogen phosphate	*n*-Heptane	Radiochemical	(*23*)
Cr^{VI}	Brines	Dithizone	Methyl isobutyl ketone (MIBK)	Atomic absorption	(*14*)
Cu	Sea water	Dithizone	CCl_4	Polarographic	(*61*)
Cu	Sea water	Sodium diethyldithiocarbamate (DEDC)	CCl_4	Spectrophotometric	(*56*)
Cu	Sea water	2,2′-Diquinolyl neocuproine	*n*-Hexanol	Spectrophotometric	(*39*)
Cu	Many trace metals		Isobutyl alcohol	Spectrophotometric	(*50*)
Fe	Many trace metals	Diphenylphenanthroline	Isobutyl alcohol	Spectrophotometric	(*50*)
Mn^{II}	Many trace metals	2-Thenoyltriflouroacetone (TTA)	Acetone-benzene	Spectrophotometric	(*13*)
Mn	Sea water	1-Nitroso-2-naphthol	$CHCl_3$	Spectrophotometric	(*39*)
Mo	Radionuclide mixture	α-Benzoinoxime	$CHCl_3$	Radiochemical	(*72*)
Mo	Brines	Dithiol	MIBK	Atomic absorption	(*14*)
Mo		2-Amino-4-chlorobenzenethiol hydrochloride	$CHCl_3$	Spectrophotometric	(*31*)
Ni	Many trace metals	Dimethylglyoxime	$CHCl_3$	Spectrophotometric	(*50*)
Pb	Environmental samples	NaI, dithizone	Isopropyl methyl ketone	Radiochemical	(*57*)
Pb	Sea water	Diethylammonium diethyldithiocarbamate	$CHCl_3$	Spectrophotometric	(*39*)
Pb	Many trace metals	Dithizone	$CHCl_3$	Spectrophotometric	(*50*)
Tl^{III}	Biological samples	NH_2SO_4 and rhodamine-B	Benzene	Spectrophotometric	(*43*)
W	Steels	8-Quinolinol	$CHCl_3$	Spectrophotometric	(*15*)
V	Many trace metals	Phosphotungstate	Isobutyl alcohol	Spectrophotometric	(*50*)
Zn	Rocks	Dithizone	$CHCl_3$	Spectrophotometric	(*27*)
Zn	Urine	Dithizone	CCl_4	Spectrophotometric	(*30*)
Co,Ni	Natural waters	Ammonium pyrrolidine dithiocarbamate (APDC)	MIBK	Atomic absorption	(*11*)
Co,Zn	Sea water	Dithizone	CCl_4	Spectrophotometric	(*19*)
Fe,Mn	Sea water	DEDC	MIBK	Atomic absorption	(*29*)
Al,Cu,Fe	Alloys	Trifluoroacetyl acetone	$CHCl_3$	Gas-liquid Chromatography	(*49*)
Cu,Mo,Zn	Sea water	8-Quinolinol	$CHCl_3$	Spectrochemical	(*7*)
Cu,Mo,Mn,V	Brines	APDC	MIBK	Atomic absorption	(41)
Cu,Fe,Mn,Ni	Brines	Cupferron	MIBK	Atomic absorption	(*14*)
Fe,Mn,Mo, Zn	Milk	APDC	$CHCl_3$	Emission spectrographic	(*63*)
Cu,Co,Ni, Pb,Zn	Tungsten	Dithizone	$CHCl_3$	X-ray spectrographic	(*26*)
Ag,Cu,Fe, Mo,Ni,V	Sea water	DEDC	$CHCl_3$	Emission spectrographic	(*73*)

Table III. Efficiency of Coprecipitation of Elements from Sea Water, Measured by Atomic Absorption Spectrophotometry

	Mn	Fe	Ni	Co	Cu	Zn
Internal std., mg./liter	5	10	5	5	5	1.25
Absorbance						
Before precipitation	0.101	0.070	0.126	0.105	0.165	0.163
	0.097	0.069	0.121	0.106	0.170	0.171
	0.099	0.069	0.113	0.104	0.166	0.161
	0.098	0.069	0.117	0.102	0.170	0.170
Av.	0.099	0.069	0.119	0.104	0.168	0.166
After precipitation	0.001	−0.002	−0.001	0.002	0.001	0.002
	0.000	0.001	0.001	0.000	0.001	0.003
	−0.001	0.000	0.003	0.000	0.001	0.001
	0.001	0.000	0.003	0.001	0.000	0.001
Av.	0.000	0.000	0.002	0.001	0.001	0.002
% coprecipitated	100.0	100.0	98.3	99.0	99.4	98.8

Metals added to acidified sea water; solution neutralized (pH 6 to 7); 50 ml. of 0.2*N* KOH added per liter.

aqueous solution, of an organic reagent which combines with the trace element of interest. The system does not require additional carrier, as is usual with the coprecipitation of a microconstituent, and is based on the principle that if a trace element and an organic reagent combine to form a compound less soluble than the reagent, then the crystallized reagent should be enriched with the trace element (*17*). In the applications to sea-water analysis described by Weiss and his coworkers, organic reagents were used which are insoluble or only sparingly soluble in water, and which form water-insoluble compounds with the trace metals of interest. They were usually added to sea water as solutions of water-miscible organic solvents, after which the mixture was evaporated to the original volume. The crystals which formed were enriched with trace elements and were large enough to be collected by rapid filtration through sintered glass. Data on quantitative recoveries of trace elements from aqueous solutions prepared in the laboratory and from sea water, at hydrogen ion concentrations practical for work with sea water, have been condensed from the papers of Weiss and his coworkers in Table I. In their work, recoveries were determined by radioactive tracers. The organic collectors used for preconcentration were not sufficiently specific for spectrophotometric measurements. Separation from interfering elements collected on the crystals required ashing, redissolution, and separation of the metallic constituents by ion exchange. Suitability of this technique for routine use aboard ships at sea was therefore limited.

The characteristics of atomic absorption spectrophotometry, recently developed as a tool for trace metal analysis, suggest that a single-stage concentration by cocrystallization may be feasible. Atomic absorption techniques are highly specific, being virtually free of spectral interferences, and chemical interferences may be frequently reduced to insignificance if reasonable care is taken with sample preparation and instrumental technique. With the atomic absorption spectrophotometers now on the market, it has been demonstrated that alcohols, ketones, and esters provide satisfactory sample matrices for the analysis of many of the transition elements (*1*). Since many of the organic reagents used for concentrating trace elements by cocrystallization dissolve readily in these solvents, it appears likely that the crystallized organic concentrate could be taken up directly and analyzed without further handling or processing—eliminating tedious separation steps and the associated risks of analytical error.

In applying this technique, the analyst should be aware that in sea water the existence of different chemical species of the elements of interest may reduce the recovery of a significant portion of the total amount in the sample.

Coprecipitation

Coprecipitation techniques have long been favored for the concentration of trace elements from sea water. Ferric hydroxide is the most commonly used carrier. Ferric salts are hydrolyzed upon addition to sea water, forming a negatively charged colloid which serves as an effective scavenger for many trace elements; it coagulates quickly and may be easily separated from the aqueous phase as a solid concentrate enriched with trace metals. The disadvantages of ferric hydroxide coprecipitation lie in the introduction of a large

Table IV. Efficiency of Coprecipitation of Elements from Sea Water, Measured by Radioactive Tracers

	Mn^{54}	Co^{60}	Zn^{65}
Internal standard, counts/min.	2260 ± 90	1170 ± 90	2730 ± 200
Recovered in precipitate	2300 ± 90	1140 ± 90	2610 ± 200
% coprecipitated	102 ± 4	97 ± 8	96 ± 7

Tracers added to acidified sea water; solution neutralized (pH 6 to 7); 50 ml. of 0.2*N* KOH added per liter.

Table V. Efficiency of Coprecipitation of Elements from Sea Water Measured by Polarography

	Cu	Zn	Pb
Internal standard, mg./liter	3.81	3.92	12.43
Concentration after precipitation	0.11	0.31	0.64
	0.16	0.28	0.60
	0.11	0.35	0.46
	0.08	0.33	0.75
Av.	0.12	0.32	0.61
% coprecipitated	96.7	91.8	95.1

Measured by Anodic Stripping Voltammetry

	Cu	Zn	Pb
Initial concentration, μg./liter	1.52	1.83	3.73
Concentration after precipitation	0.15	0.20	0.04
	0.12	0.09	0.60
	0.08	0.12	0.29
	0.17	0.28	0.29
	0.06	0.15	0.41
Av.	0.12	0.17	0.33
% coprecipitated	92.1	90.7	91.1

quantity of iron into the sample with the attendant difficulties of heavy-metal contamination from the reagent and of removing the excess iron prior to analysis. Hydrated oxides of aluminum, rare earths, and manganese also have been used as carriers, but these are subject to the same kinds of disadvantages.

For the activation analysis of Mn and Zn, Rona *et al.* (*47*) coprecipitated these elements from sea water with ferric hydroxide. The pretreatment prior to activation involved a double reprecipitation to remove occluded major ions, and extraction with isopropyl ether to remove iron. They regarded Mn and Zn separated in this manner as "total" in contrast to "divalent" ionic species separated by solvent extraction.

For the colorimetric determination of manganese, iron, and copper from sea water, Skopinstev and Popova (*52*) concentrated their samples by coprecipitation with mercurous sulfide. The mercury was easily removed by ignition of the precipitate at 450° C.

Following the lead of Koroleff (*32*) who determined manganese, Laevastu and Thompson used the natural collectors present in sea water for the coprecipitation of nickel (*35*) and cobalt (*60*). When the pH of a sample of sea water is raised to about 12, the alkaline earth hydroxides and carbonates which are precipitated are effective scavengers for many heavy metals. Koroleff used potassium hydroxide, and Laevastu and Thompson preferred sodium carbonate for raising the pH of the sample. The precipitates were redissolved in acid, and the metals of interest were determined colorimetrically after separation from interfering substances carried down with the precipitate. Loveridge *et al.* (*39*) criticized the method for use in the determination of manganese because of difficulty in handling the bulk of precipitate obtained with large samples. However, in our experience, quantitative recovery of six transition elements from sea water does not require precipitation of all of the magnesium in the sample for the carrier phase; and 10 mg. of precipitate per liter of sea water is sufficient.

A procedure for separating Co, Ni, Mo, Fe, Pb, Sn, Zn, V, Ti, Cr, and Ag from phosphates, alkalies, and alkaline earth metals in plant materials and soils and concentrating them for spectrographic analysis was developed by Mitchell and Scott (*44*). The trace elements were coprecipitated with a mixture of 8-quinolinol, tannic acid, and thionalide. Aluminum and iron were added as carriers. Black and Mitchell (*6*) applied this technique to the spectrographic determination of trace elements in sea weeds and sea water.

Solvent Extraction

Solvent extraction systems have been widely used for concentrating trace elements from sea water. With the proper choice of reagents, an extraction may be selective for either a narrow or a broad range of elements to be transferred from sea water to a solvent concentrate suitable for the analytical system to be used.

A selection of solvent-extraction systems, which either have been, or could be, used for sea water analysis is presented in Table II. In some systems, the extractions are sufficiently specific for the separation of an element for determination by a nonselective analytical system. In others, groups of elements are extracted for simultaneous or successive determinations by more selective analytical systems.

The separation of inorganic ions from aqueous media by phase-distribution procedures has been considered by West (*70*). By selection of appropriate ion-association and chelate solvent systems, almost all of the elements may be extracted from aqueous solutions.

The applicability of a solvent extraction technique to a given analytical system will depend on the properties of the trace element-reagent association and of the solvent. The absorption spectrum of an ion-association compound, complex, or chelate of a metal can often be used for spectrophotometric determination if the solvent does not absorb strongly at the selected wavelength. Combustion properties and viscosity must be considered in choosing solvents for use in emission and atomic absorption systems in which flames carry the sample into the optical path.

Systems in which sequestered trace elements are extracted

Table VI. Efficiency of Extraction of Elements as Diethyldithiocarbamates from Aqueous Solution into Methyl Isobutyl Ketone

(Measured by atomic absorption)

	Mn	Fe	Ni	Co	Cu	Zn
Internal std., mg./liter	5	10	5	5	5	1.25
Absorbance						
Before extraction	0.195	0.153	0.114	0.115	0.216	0.245
	0.195	0.152	0.110	0.117	0.212	0.235
	0.193	0.155	0.111	0.117	0.220	0.247
	0.199	0.155	0.114	0.124	0.211	0.247
Av.	0.195	0.154	0.112	0.118	0.215	0.244
After extraction	0.001	−0.001	0.001	0.000	0.000	−0.002
	0.002	0.000	0.001	−0.002	0.000	−0.002
	0.001	0.000	0.001	0.000	0.001	−0.005
	0.001	−0.001	0.000	−0.001	0.000	−0.006
Av.	0.001	−0.001	0.001	−0.001	0.000	−0.004
% extracted	99.5	100.6	99.1	100.8	100.0	101.6

Metals added to acidified solution; pH adjusted to 6, concentration of DEDC to 0.25%; extracted for 1 minute with MIBK (10 to 1 aqueous to organic).

into chloroform have been widely used. Chloroform solutions can easily be evaporated to adjust the volume of the concentrate to the capacity of spectrophotometer cells, to deposit residues on spectrographic electrodes or planchets used for x-ray and nuclear irradiation and detection, and to provide a solid residue for ashing and redissolution in aqueous media for analysis by electroanalytical or other methods.

Substituted dithiocarbamates appear to be particularly useful for the separation of heavy metals in natural waters. Malissa and Schöffmann (*40*) have studied the color, sensitivity, and selectivity of the reaction products of 30 metal ions with various dithiocarbamates. Lakanen (*37*) extracted 18 trace elements into chloroform with pyrrolidine dithiocarbamic acid and analyzed the evaporated residues by emission spectroscopy. Slavin (*53*), who recently summarized the available data on the use of ammonium pyrrolidine dithiocarbamate (APDC) for the extraction of many heavy metals, cited references for Cu and Zn in fertilizers, plants, and soils; for Pb, Bi, Hg, Ni, and Sb in urine; for Cu, Pb, Cd, Fe, Mn, Co, and Ni in brines; and for Cu in milk and silicate rocks.

Countercurrent and continuous-extraction processes have promise for application to sea water. A true countercurrent extraction apparatus employing compact cells and capable of continuous, large scale operation is under development by Penniston and Johnson (*45*). Brooks (*8*) has reported a system for extracting and separating trace elements from silicate rocks. His liquid-liquid discontinuous countercurrent extractor separated 17 elements, including some only weakly extracted by ordinary methods. The separation of different oxidation states of the same metal was noted. In another application of this procedure (*9*), he used countercurrent extraction for concentrating Mn, Pb, Mo, Sn, Ni, Al, V, and Ag from sea water into a solution of oxine in chloroform. An enrichment factor of 400,000 was obtained and many of the elements could be determined easily by emission spectroscopy.

Two-Stage Concentration

If the analytical system employed for a particular analysis is sufficiently specific, the technique used for concentrating the samples need not be highly selective. Indeed, for multielement analyses, it is desirable to use methods of concentration that will separate large groups of trace elements from the original sample.

For use aboard ships at sea, we have developed a technique to produce a concentrate which can be processed readily for either atomic absorption or polarographic analysis. Trace elements are initially coprecipitated by adding 50 ml. of $0.2N$ KOH or 5% Na_2CO_3 per liter of sea water to samples ranging in volume from 4 to 50 liters. After stirring for 1 hour and settling overnight, the precipitate is collected on a fine-porosity, sintered-glass filter and redissolved in acid. At this point, the concentrate may either be stored in polyethylene bottles or processed further, if analysis is to be performed aboard ship. For a second stage of concentration, the pH of the concentrate is adjusted to 6.0 and enough 5% sodium diethyldithiocarbamate (DEDC) added to make a 0.25% solution. Heavy-metal dithiocarbamates are transferred to an organic phase consisting of methyl isobutyl ketone (MIBK) by a single extraction at a 10 to 1 aqueous to organic ratio. At this stage, the concentrate may be used without further treatment for atomic absorption measurements, as the MIBK provides an excellent matrix for flame analysis. Addition of 1 part of acetone to 5 parts of the concentrate absorbs water droplets entrained in the organic phase. For polarographic measurements, the solvent (amyl alcohol) is evaporated under vacuum; the residue is wet-ashed, converted to the chloride form, and redissolved in distilled water. With this technique, 1000-fold concentration was achieved with the concentrate in a form suitable for conventional polarographic measurement of Cu, Pb, Zn, Fe, and Mn.

Recoveries of trace elements obtained with each of the two steps of the concentration procedure were determined by radiometric, atomic absorption, conventional polarographic, and anodic stripping analyses (Tables III to VI). The use of anodic stripping voltammetry for trace analysis of brines (*2*) opens a promising avenue of approach to the analysis of sea waters. The measurements shown in Table V (lower) were made on raw sea water taken from a depth of 20 meters from Sooke Inlet on the west coast of Vancouver Island, Canada, which because of industrial pollution is not necessarily representative of open ocean water.

Sorption

Sorption methods have long been used for the removal of substances from dilute solutions and, with the advent of radioactive isotopes, have been invaluable for concentration and separation of radioactive mixtures by column chromatography. Chromatographic techniques for the isolation of fission products and other radioactive substances from natural waters have been widely reported in the literature of radiochemistry and need not be repeated here. Several new techniques involving sorption phenomena currently being developed, however, show much promise of usefulness for trace metal characterization of sea waters.

Carritt (*12*) has proposed and tested a chromatographic procedure for concentrating heavy-metal ions from sea water. A strongly basic anion-exchange resin is charged with dithizone in basic solution and packed into a column. Sea water is then passed through the column, which retains ions of those metals which form metal dithizonates in slightly basic solution. The drawbacks to this technique are: To ensure quantitative recovery of the largest number of dithizone-reacting metals, a slow rate of flow is required which extends the time for processing large samples; a large quantity of concentrated acid is required to elute the absorbed metals from the column; and it shares with all other concentration schemes which employ binding of ions in sea water by sequestering agents, the disadvantage that competition by natural sequestering agents in sea water may affect the recovery of the ions in question.

More recently, Bauman (*3*) has developed a technique for preparing a dithizone-coupled cellulose column for which he claims substantial reduction in the first two disadvantages listed above.

Although the cation-exchange properties of the ammonium salts of some heteropoly acids have been known for over 50 years (*4*, *10*, *20*, *42*, *58*, *59*), it has been only recently that microcrystalline aggregates of these inorganic salts have been used for the selective adsorption of alkali, alkaline earth, and some transition metals (*34*). The use of ammonium molybdophosphate (AMP) crystals for the separation of alkali metals has been described by Smit *et al.* (*54*, *55*) and in recent United Kingdom Atomic Energy Agency reports (*62*).

In our laboratories, preliminary experiments with batch methods effected quantitative transfer of rubidium and cesium from solution in 1 liter of acidified sea water (pH 2) to 1 gram of AMP microcrystals. Recovery was determined by radiometric measurement of Cs^{137}, and atomic absorption measurement of stable Rb added as internal standards.

For reasonably precise (<5%) flame emission or atomic absorption measurements of Rb and Cs, solutions containing 5 to 50 p.p.m. of each are recommended (*5*, *18*). Batch treatment of 1 liter of sea water with AMP should be sufficient to produce a 10-ml. concentrate containing about 12 p.p.m. of Rb, but 40 liters of sea water would be necessary to provide enough Cs for a 10-ml. concentrate of about 8 p.p.m. Rb, and Cs adsorbed on AMP can be eluted with NH_4NO_3 or the crystals can be dissolved with dilute NH_4OH to provide the liquid concentrate.

Summary

Although several analytical systems of great sensitivity have been applied to the direct analysis of sea water, adequate precision and accuracy for reliable trace characterization can best be achieved by concentration before analysis.

Complete recovery, in a concentrate of a heavy metal trace element, whatever its physically or chemically combined state in sea water, can usually be obtained by removal of the water from the sample. Selective coprecipitation permits much greater concentration factors and quantitative recovery of many trace elements as well as separation from the major salts. Care must be taken to avoid introduction of contamination with the reagents added to effect the precipitation. Trace elements in the ionic state in sea water may be concentrated by cocrystallization and solvent extraction procedures involving the use of organic sequestering agents.

We have found that two-stage preconcentration, by coprecipitation and solvent extraction, is useful for preparation of sea-water samples for atomic absorption and polarographic analyses. Alcohol, ketones, and esters make effective matrices for the analysis of concentrates by atomic absorption.

Heavy alkali-metal ions may be adsorbed onto ammonium molybdophosphate microcrystals to separate them from the major salts of sea water and to provide concentrates suitable for determination of both radioactive and stable species.

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Nutrient Budget: Rational Analysis of Eutrophication in a Connecticut Lake

Charles R. Frink

Department of Soils and Climatology, The Connecticut Agricultural Experiment Station,
New Haven, Conn.

■ The significance of nutrient contamination of water by man can be evaluated only by comparison with all other sources. In an exemplary eutrophic lake in northwestern Connecticut, the nutrient input from a largely forested watershed with no overt source of pollution was adequate to support the observed abundant vegetative growth. In addition, a vast accumulation of nutrients was found in the lake bottom sediments; the upper centimeter of sediment contains at least 10 times the estimated annual input of nitrogen and phosphorus. Moreover, this reservoir of nutrients in the sediments should be capable of supporting plant growth for some time even if all nutrients could be excluded from the lake. Apparently, the abundant weeds and algae in this lake are the result of natural eutrophication which man will be hard pressed to alter.

In our current concern with the nutrient pollution by man of his water supplies, we are apt to overlook the fact that natural enrichment, or eutrophication, is a spontaneous process which begins as soon as a lake is formed. Thus, to determine whether man is accelerating this process, we must compare his contribution with all other nutrient sources. An analysis is reported here of the nutrient sources for an exemplary, shallow, weedy lake that frequently supports abundant algae.

Bantam Lake, located in northwestern Connecticut, covers an area of 370 hectares, contains about 16×10^9 liters, and has an average depth of 4.4 meters. It is elongated in shape, with a North and South Bay connected through a larger central bay. Both the inlet and outlet are located in North Bay, but dye and float experiments indicate that extensive mixing occurs with the rest of the lake. The watershed covers 8500 ha. and at one time contained a large number of dairy farms. A land use survey in 1954 showed about 50% of the area was forested; the remainder was mixed tillage, pasture, and abandoned fields. Abandonment has continued, and today the area is typical of the rural environment surrounding many other lakes in the state. The population of the watershed is about 10,000 people, with about 7500 located in a town near the inlet to the lake. This town's sewage treatment plant, which serves about 2500 people, discharges its effluent largely to groundwater near the inlet.

Methods and Results

Analysis of Sediments. The quantity of nutrients available from sediment was estimated first. Bottom samples were collected from Bantam Lake using both a core sampler and an Ekman dredge. Only a few cores were taken, but they indicate that the organic sediments grade within a depth of 1 to 2 meters into sandy strata. At an estimated rate of sedimentation of 250 years per meter (Hayes, Reid, *et al.*, 1958), however, it appears that eutrophication was occurring before man's intervention.

The clay fraction smaller than 2 microns in both the core and dredge samples was similar mineralogically to the clay present in soils of the watershed. However, none of the sediment vermiculite contains Al-interlayers; possibly, the neutral lake environment has altered the interlayered vermiculite in the surrounding acid soils (Frink, 1965).

Bottom mud collected with the dredge was analyzed for loss on ignition and total N by conventional methods. As might be expected, the samples (Table I) rich in organic matter are also rich in total N; in fact, the correlation coefficient between loss on ignition and total N was 0.99. In addition, total N increases with increasing depth of water as has been reported (Hasler, 1963) for sediments in Lake Mendota. This may merely be another indication of increasing organic matter with depth. The C:N ratio tends to decrease with increasing depth, however, indicating that the increase in N with depth is both an increase in organic matter and enrichment in N of that organic matter.

The P in the sediments was fractionated according to a differential dissolution scheme (Chang and Jackson, 1957). The total P (Table I) tends to increase with increasing depth as in Lake Mendota (Hasler, 1963), largely because of an increase in inorganic P. Fractionation of these samples showed that most of the P was contained in the Fe and Ca phosphate fractions. However, the NH_4F soluble or so-called Al phosphate fraction in soil clays has been shown (Weir and Soper, 1961) to equilibrate readily with P^{32} and is generally assumed to be more available for plant growth. In these samples, the Al phosphate fraction increased with depth, both absolutely and as a proportion of the total inorganic P. Thus, the sediments in deeper water contain more P and an increasing proportion of this P is readily exchangeable.

Apparently, the center of the lake acts as a reservoir for both total and available N and P. The N in the sediments is mostly in organic form, while P occurs largely in inorganic forms. The depth of sediment capable of supplying nutrients remains unknown. The top several centimeters of sediment in Bantam Lake are approximately a 10% suspension; thus, the stirring discussed by others (Hayes, Reid, *et al.* 1958; Gorham, 1958) suggests that several centimeters of mud are capable of supplying nutrients to the water. One

Table I. Analyses of Bottom Mud Samples Collected from Bantam Lake

Sample No.[a]	Depth Water, M.	Organic Matter, %	Total Nitrogen, %	Phosphorus, %		
				Inorganic[b]	Organic[b]	Total
A 18	7.0	27.3	1.44	...	...	0.270
J 9	6.4	28.7	1.46	0.180	0.030	0.210
J 8	6.1	28.5	1.44	0.132	0.068	0.200
J 7	6.1	23.3	1.18	0.153	0.047	0.200
J 14	6.1	25.9	1.24	0.173	0.017	0.190
J 6	5.2	26.8	1.36	0.160	0.040	0.200
J 15	5.2	26.3	1.28	0.130	0.050	0.180
J 10	4.9	27.0	1.40	0.191	0	0.190
J 2	4.3	26.8	1.32	0.185	0.015	0.200
F 4	4.3	14.6	0.80	...	...	0.180
J 3	4.0	28.8	1.40	0.141	0.069	0.210
J 1	3.4	24.7	1.20	0.102	0.068	0.170
J 11	3.4	14.4	0.74	0.160	0	0.140
J 4	3.0	25.0	1.16	0.097	0.083	0.180
F 2	3.0	26.7	1.44	...	...	0.280
J 5	2.1	19.5	0.96	0.121	0.149	0.270
J 13a	1.8	11.7	0.50	0.094	0.006	0.100
J 13b	1.8	13.3	0.58	0.052	0.048	0.100
J 12	1.5	1.0	0.08	0.041	0	0.040
A 17	1.2	15.1	0.72	...	...	0.140
A 16	1.2	10.6	0.36	...	...	0.100
A 19	1.2	1.9	0.16	...	...	0.070
A 20	0.6	2.1	0.12	...	...	0.170

[a] F = February 22, 1966. J = June 27, 1966. A = August 29, 1966.
[b] Not determined.

centimeter of this sediment seems a conservative estimate of the region of exchange; this 1 cm. contains the amounts of N and P shown in Table II, calculated from the average concentrations in the sediment at the mean depth of the lake.

Analysis of Weeds and Algae. The nutrients stored in weeds were determined by chemical analyses and yield estimates. Samples of eight common aquatic weeds were collected at the end of August, washed, dried, ground, and analyzed. The average nutrient contents were 3.02% N and 0.43% P. These may be compared with the critical levels recently reported (Gerloff and Krombholz, 1966) for several similar species—1.3% N and 0.13% P. In several infertile Wisconsin lakes, weeds contained less than the critical level of P; by contrast, our weeds seem well nourished. Yields of weeds in Bantam Lake were estimated by making a number of casts with a rake. Although the results were quite variable, the average yield of dry matter was approximately 900 kg. per ha. About twice this yield has been reported (Hasler, 1963) for weeds in Lake Mendota. Weeds were estimated to extend out to the 2-meter contour, which includes about 25% of the lake area; thus, the weeds contain the nutrients shown in Table II.

The nutrients in a standing crop of algae can be estimated from data of Adamson (1963). In four Connecticut lakes during bloom, she found 1.8 p.p.m. of total N and 150 p.p.b. of total P. Since algae are about 7% N and 0.7% P, this would correspond to a yield of dry matter of about 900 to 1100 kg. per ha., somewhat higher than in Wisconsin lakes (Hasler, 1963). Thus, a heavy algal bloom would contain the nutrients shown in Table II.

Analysis of Water. The nutrients stored in the lake water, as well as contributions from the watershed, were determined from water analyses for total N and P. Water samples were collected biweekly, commencing May 13, 1966, from three stations in the lake. Each station was sampled at the surface, 2 meters down and 1 meter from the bottom. Neither the differences among locations at any one station nor the differences among stations were significant; the means for 10 sampling dates at these lake stations (LA, LB, LC) are shown in Table III. The grand mean for all three stations was 0.66 p.p.m. of N and 35 p.p.b. of P. Benoit (1965) found 0.63 p.p.m. of N and 23 p.p.b. of P in surface samples from these same stations for eight sampling dates in 1963 to 1964; thus, the nutrient content of the lake water during the growing season is reasonably well established. Using the ob-

Table II. Nitrogen and Phosphorus Budget of Bantam Lake

Inventory Item	N, Kg./Lake	P, Kg./Lake
In 1 cm. of sediment	44,000	7400
In aquatic weeds	2,500	360
In algal bloom	29,200	2430
In lake water	10,700	460
Input from watershed	30,700	2100
Output from lake	−27,500	−1970
Mean net input	+3,200	+130
Maximum net input	+6,000	+1700

served mean concentrations, we conclude the lake contains the nutrients shown in Table II.

The nutrients from the watershed were determined by analyses of samples from four stations: WS, a tributary stream in the watershed; UP, upstream and DWN, downstream from the treatment plant on the inlet; and OUT, the lake outlet. Samples were taken biweekly commencing May 13, 1966. Differences among stations were not significant; the grand mean for all watershed stations was 0.52 p.p.m. of N and 37 p.p.b. of P. These agree reasonably well with previous analyses (Benoit, 1965) of samples from the same stations for six dates: 0.42 p.p.m. of N and 34 p.p.b. of P. Also, these analyses may be compared with those from pan lysimeters under a stand of mixed hardwoods (Lunt, 1941). Over a 2-year period, the leachate through duff and soil contained about 1.2 p.p.m. of N and 50 p.p.b. of P. The forest alone could supply the amounts of N and P found in the water.

The relatively large variability observed (Table III) in nutrient concentration in water both from station to station and from time to time is a source of some concern. An analysis of variance of the data for the lake and watershed combined, as well as for the watershed stations only, showed no significant differences among stations for either N or P. However, in all cases, the differences within stations—i.e., from time to time—were highly significant, with the P concentration being more variable than N. Replicate analyses of replicate samples indicated that the analytical techniques were satisfactory. Significant differences were observed in the P concentration of grab samples taken at approximately 5-minute intervals at the same station. Differences in N concentrations were smaller and not significant. Some of the remainder of the variability in P concentrations can be attributed to rainfall—as rainfall increases, so does P concentration, apparently owing to an increase in suspended or particulate P. Perhaps this particulate P is also responsible for the sampling variability encountered. Obviously, an elaborate sampling program, using either composite or proportional samplers, combined with stream flow measurements (Bormann and Likens, 1967), would be required to improve these analyses materially. It is doubtful, however, that this would materially improve the estimated budget, since the annual net input from the watershed is obviously small.

Although the input from the watershed is small, the nutrients available from this source must be considered. The runoff from the watershed can be estimated from Shackham Brook in New York (Penman, 1963). The vegetation was mixed old field, the rainfall about 107 cm. per year (1934–47), and the runoff about 66 cm. per year. Thus, the 8500 ha. watershed will pour about 56 × 10^9 liters into the lake, or about 3.5 times its capacity. The flow in the inlet has been estimated to be about 40 × 10^9 liters annually; thus, this assessment of the total input from the watershed seems reasonable. Using the mean concentrations of 0.52 p.p.m. of N and 37 p.p.b. of P, the nutrient input is shown in Table II. In addition, approximately 1800 kg. of N and 30 kg. of P would be added by direct precipitation on the lake. Finally, evaporation from the lake amounts to about 5% of the total flow, so the nutrient output is reduced correspondingly.

Discussion

Apparently (Table II), the watershed contributes enough nutrients to support the observed growth of weeds as well as a heavy algal bloom. Moreover, this input comes from a watershed which is largely forested, with no overt source of pollution. Thus, this analysis casts considerable doubt on the assumption frequently made that our lakes were clear before man's intervention. The abundant vegetative growth in this lake is apparently the result of the naturally occurring process of eutrophication.

The observation that the inlet, lake, and outlet are all at the same nutrient concentration requires closer examination. If the assumed sedimentation rate of approximately 4 mm. per year is correct (Hayes, Reid, *et al.*, 1958), then the nutrients sedimented per year are, of course, 40% of those shown in Table II for the upper 1 cm. of sediment. These amounts are approximately equal to the annual input to the lake from the watershed and seemingly would require that the concentrations in the outlet be zero. This was not observed, and thus the source of these sedimented nutrients is uncertain.

The maximum error introduced by analytical uncertainties was estimated as follows: The 95% fiducial limits for the difference between the mean N concentration at the inlet and outlet—i.e., DWN − OUT = −0.10—are +0.05 to −0.24 p.p.m. of N. This suggests that the lake is likely to be losing N, but, if we use the upper positive limit, the lake could be gaining 2800 kg. of N annually. Similarly, the 95% fiducial limits for the difference between the mean P concentration at the same stations are +28 to −20 p.p.b. If we use the upper limit, the lake could gain 1570 kg. of P annually. Thus, the annual net input could be as large as 6000 kg. of N and 1700 kg. of P (Table II), or about 35% of the N and 60% of the P in the 4 mm. of sediment assumed to accumulate annually. Thus, it seems that the maximum sedimentation rate in the lake would be closer to 1 to 2 mm. per year, which is similar to the estimated rate of formation of sedimentary peat bogs of 0.6 mm. per year (Dawson, 1956).

Conversely, if the present data, which indicate that the lake has reached equilibrium, are accepted, one might inquire if they are consistent with the presumed course of natural

Table III. Analyses of Water from Bantam Lake and Watershed

Station	WS	UP	DWN	LA	LB	LC	OUT
Total N, p.p.m.	0.45	0.51	0.51	0.69	0.64	0.65	0.61
No. of observations	16	16	18	27	28	30	17
Standard error	0.05	0.05	0.05	0.04	0.04	0.04	0.05
Total P, p.p.b.	35	33	42	40	30	36	39
No. of observations	16	16	18	27	30	29	17
Standard error	8	7	6	5	5	6	10

eutrophication. Starting at a low level of fertility, the concentration of nutrients in lake water would gradually increase until some upper limit is imposed. In the case of N, this limit is biological—i.e., the ability of microorganisms in the sediments to retain N while decomposing the freshly sedimented organic matter. Little is known of the C:N ratio of lake sediments; sedimentary peats and mucks, however, had a C:N ratio of about 20 to 1 (Feustel and Byers, 1930). In Bantam Lake sediments, the C:N ratio is also about 20 to 1; thus, it seems that an equilibrium may have been reached.

An upper limit on the concentration of P may be imposed by the solubility of Fe, Al, or Ca phosphates, depending on the pH. In Bantam Lake, with the water at about pH 7, we might expect one of the Ca phosphates, either hydroxyapatite or fluorapatite, to precipitate. Indeed, calculations show that Bantam Lake water is slightly undersaturated with respect to hydroxyapatite but is very close to the value predicted for equilibrium with fluorapatite (Murrman, 1966).

Thus, it seems that natural eutrophication would produce increasing nutrient concentrations until these limits are reached. Assuming that the same chemical processes occur in the streams (at least near the inlet and outlet where the present samples were taken), concentration differences would be small and difficult to detect. The net annual nutrient input would then appear to depend largely on the nutrients in rainfall and differences between the volume of incoming and outgoing water.

If this is so, what is the source of nutrients supporting the observed abundant plant growth? Assuming a sedimentation rate of 1 mm. per year, about 4400 kg. of N and 740 kg. of P are required. The nutrients in rainfall and those left owing to evaporation amount to 3200 kg. of N and 130 kg. of P (Table II). Clearly, in these terms, P is in much shorter supply than N. This, then, supports the concept that P must be recycled within the lake many times during the growing season. The source of the P must, of course, be the sediments. From Table II, the mere upper 1 cm. of sediment contains several times as much N and P as that required to support the observed growth of weeds as well as a heavy algal bloom. Further, the N:P ratio of the sediments is about 6 to 1, while that observed in sedimentary peats of about the same N content is approximately 25 to 1 (Feustel and Byers, 1930). Thus, fresh lake sediments are relatively rich in P when compared with the bogs they will ultimately become, and it is therefore reasonable to suppose that as eutrophication proceeds, the P stored in the sediments can serve as a source of nutrients.

The availability of these nutrients is unknown; the calculations presented so far have assumed that all the nutrients in the water are available. This is probably a reasonable assumption for water, but it surely is not true of the sediments. By analogy to soil, approximately 5% of the N and 0.5% of the P would be available for plant growth. Thus, the upper 1 cm. of sediment could supply 2200 kg. of N and 37 kg. of P. Again, P is in short supply. The weeds in Bantam Lake apparently are not P deficient, which suggest that perhaps much greater depths of sediment are capable of supplying P.

These estimates of nutrient availability in turn raise another very important question: Is eutrophication reversible? In other words, if the input of nutrients from the watershed of Bantam Lake were completely stopped (which is manifestly impossible), would the lake continue to produce weeds and algae? Clearly, the answer to this question lies in the ability of the sediments to supply nutrients, particularly P, to the water.

Summary and Conclusions

An analysis of the nutrient sources for a typical weedy lake in northwestern Connecticut, which frequently supports abundant algae, reveals two important aspects of eutrophication. First, it is evident that the nutrient input from a largely forested watershed with no overt source of pollution is adequate to support the observed abundant vegetative growth. This analysis, as well as the observed depth of sediment, casts some doubt on the frequent assumption that Connecticut's lakes were clear before settlement. Second, the nutrients which accumulate in bottom sediments as eutrophication proceeds constitute a vast reservoir apparently capable of supporting plant growth in the event the input is shut off. The implication of this conclusion for lakes suffering from additional contamination by man is serious: Will expensive efforts to prevent this man-made contamination actually reverse eutrophication and clean up our lakes? The present data indicate that the answer to this question lies in the ability of sediments to supply nutrients, particularly P, to the water.

Acknowledgment

Water sampling and analyses were performed by the Henry Souther Engineering Co., Hartford, to which I am grateful for their cooperation. In addition, much assistance in weed and sediment sampling and analyses was provided by my colleagues. Finally, Paul E. Waggoner has generously contributed much helpful discussion and criticism of the ideas presented here.

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Earthy-Smelling Substance from a Blue-Green Alga

Robert S. Safferman, Aaron A. Rosen, Charles I. Mashni, and Mary E. Morris
U. S. Department of the Interior, Federal Water Pollution Control Administration, Cincinnati, Ohio 45226

■ The blue-green alga *Symploca muscorum* produces an earthy-smelling metabolite at an estimated concentration of 0.6 mg. per liter of culture medium. The substance has been isolated by preparative gas chromatography and identified as geosmin on the basis of direct comparison with an actinomycete-produced standard. The results suggest that organisms other than actinomycetes are possible sources of earthy taste and odor problems in water supplies.

Actinomycetes produce a characteristic earthy odor (Waksman, 1959) which led to their early indictment as a cause of earthy taste and odor problems in water supplies (Adams, 1929; Thaysen, 1936). Recent studies (Silvey, Russell, *et al.*, 1950; Silvey and Roach, 1956) have again directed attention to the effect of these organisms on water quality. Gerber and Lechevalier (1965) recently isolated a specific compound having this earthy odor from the metabolic products of several *Streptomyces* strains. The compound, which was named geosmin, was characterized as a colorless neutral oil with an indicated molecular formula of $C_{12}H_{22}O$ and an approximate boiling point of 270° C. (Gerber and Lechevalier, 1966).

During routine transfer of a stock culture of the filamentous blue-green alga *Symploca muscorum* strain IU 617 (Indiana University culture collection), an earthy odor was perceived, indistinguishable from that of an actinomycete culture studied previously (Romano and Safferman, 1963). The odorous substance, which was isolated and shown to be identical to the geosmin produced by actinomycetes, is apparently the first example of such a compound in an alga.

Materials

Symploca muscorum IU 617 was cultured in a modified Chu No. 10 nutrient medium: $Ca(NO_3)_2 \cdot 4H_2O$, 0.232 gram; K_2HPO_4, 0.01 gram; $MgSO_4 \cdot 7H_2O$, 0.025 gram; Na_2CO_3, 0.02 gram; $Na_2SiO_3 \cdot 5H_2O$, 0.044 gram; ferric citrate, 3.5×10^{-3} gram; citric acid, 3.5×10^{-3} gram; $CuCl_2 \cdot 2H_2O$, 1×10^{-7} gram; $CoCl_2 \cdot 6H_2O$, 2×10^{-5} gram; $ZnCl_2$, 4×10^{-4} gram; $MnCl_2 \cdot 4H_2O$, 1.4×10^{-3} gram; H_3BO_3, 2.4×10^{-3} gram; distilled water, 1000 ml.

The purity of the algal culture was determined employing the following media: modified Chu No. 10 nutrient medium (Chu) + 0.1% sodium glutamate; Chu + 0.1% glucose; Chu + 0.1% proteose; Chu + 0.2% maltose; Chu + 0.2% starch; soil extract medium: 4% garden soil-water supernatant in Bristol's solution (Starr, 1964); yeast extract, nutrient, and egg albumen media (Safferman and Morris, 1962); starch-casein medium (Kuster and Williams, 1964); neopeptone-dextrose and diamalt media (Cooke, 1963).

An authentic sample of geosmin was supplied by N. N. Gerber, Rutgers, The State University, New Brunswick, N.J.

Culture Methods

The alga was routinely cultured in 250-ml. Erlenmeyer flasks containing 100 ml. of modified Chu No. 10 nutrient medium. Each flask was inoculated with 5 ml. of stock culture, the matted filaments of which had been first dispersed by aseptically homogenizing them for 5 seconds in a Waring Blendor. Incubation was carried out for 15 to 20 days at 20° C. "Cool white" fluorescent tubes provided illumination of 160 to 180 foot-candles. Large-scale culturing for isolation of geosmin was carried out aseptically in 5-gallon carboys which were illuminated at 400 to 500 foot-candles and vigorously aerated.

Bacterial contamination of the unialgal culture could be readily demonstrated by use of several media. However, no actinomycetes or fungi could be detected microscopically or isolated from the algal culture. Attempts to free the organism from bacteria by isolating the algal filaments on agar (Lewin, 1959) removed only part of the bacterial contaminants; consequently, an examination was undertaken of the odor contribution of the contaminating bacteria originally present. These bacteria were isolated on agar and each was cultured at 22° to 25° C. for 14 days. The cultures were examined periodically for development of odor. In no instance was a perceptible earthy odor produced in any of the test media. Evidently, the bacterial contaminants could not be a primary source of the earthy odor.

Results and Discussion

No apparent differences in geosmin production were shown between the original and partially purified algal cultures. In the latter cultures, traces of bacterial contaminants were revealed as minute pellets, present only in glutamate- or peptone-supplemented Chu medium. These bacteria apparently constitute an infinitesimal portion of the biomass, since microscopic examination of the culture consistently failed to reveal their presence. These facts strongly imply that the alga is responsible for the earthy odor.

Twenty-four liters of culture were pooled and immediately distilled at atmospheric pressure until about 20% of the volume was collected. The distillate was then extracted six times with a total volume of 4 liters of anhydrous ethyl ether. Only negligible quantities of the earthy odor remained in the

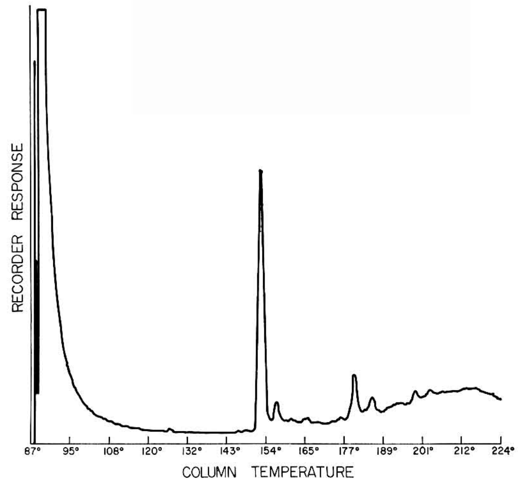

Figure 1. Gas chromatogram of 1.0 μl. of earthy odor concentrate from *Symploca muscorum*

Column (1.8 meters × 3.2 mm.) containing 20% SE-30 on 60- to 80-mesh Chromosorb W; temperature programmed at 6° C. per minute; dual flame ionization detector

water. The odor material was further concentrated by evaporating the ether extract to a final volume of 0.5 ml. under a stream of dry air.

Gas chromatography (Figure 1) showed that the concentrated extract contained many detectable components. By peak-area analysis, however, the single strong peak of geosmin eluting at 153° C. represented 75% of the total metabolites recovered. The principal component, isolated by preparative gas chromatography, had an intense earthy odor. An odor panel determined that its threshold odor concentration in water was 0.2 p.p.b., which accounted for most of the odor of the concentrated extract.

The isolate was identified as geosmin on the basis of the following comparisons with an authentic sample:

An odor panel judged the odor qualities of both substances to be identical.

Their threshold odor concentrations of 0.16 *vs.* 0.2 p.p.b. (based on estimated weights determined by relative peak areas) were equal within the precision of this measurement.

The retention times of the algal isolate matched those of the geosmin reference on three different gas chromatographic columns (SE-30, Apiezon L, and diethylene glycol adipate).

The infrared spectrum of the algal isolate matched that of geosmin (Gerber and Lechevalier, 1966)—points of similarity were the absence of hydroxyl, carbonyl, olefinic, and aromatic bands and the presence of identical prominent bands at 6.9, 7.25, 7.95, 8.6, 9.15, 9.5, 9.8, 10.0, 10.3, 10.6, 10.9, 11.3, and 11.8 microns.

The odor intensity of the algal isolate was reduced by a factor of 2000 when it was treated with HCl in methylene chloride in a procedure which is known to destroy geosmin (Gerber and Lechevalier, 1965).

Based on peak-area analysis of the ether concentrate, the yield of geosmin was 0.6 mg. per liter of pooled algal culture. This yield is comparable with that obtained from various species of *Streptomyces* (Gerber and Lechevalier, 1965). Accordingly *Symploca muscorum* and possibly other algae are potential sources of earthy taste and odor problems in water supplies.

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COMMUNICATION

Microdetermination of Peroxides by Kinetic Colorimetry

Thomas C. Purcell and Israel R. Cohen
Bureau of Disease Prevention and Environmental Control, Public Health Service, Cincinnati, Ohio

■ Ferrous thiocyanate, neutral potassium iodide, and molybdate-catalyzed potassium iodide reagents were used for the analysis of microgram quantities of a variety of peroxidic compounds by kinetic colorimetry. Ozone and peracetic acid gave an immediate maximum color development with all three reagents. Hydrogen peroxide gave slow color development with neutral KI only. Acetyl peroxide, nitrogen dioxide, alkyl hydroperoxides, and peroxyacyl nitrates gave slow color development with all three reagents. The half lives of these colorimetric reactions were used to identify specific oxidants.

The occurrence of ozone, peroxyacetyl nitrate, and nitrogen oxides in polluted atmospheres is, of course, well known. Haagen-Smit (1952) has reported the presence of peroxides in California smog. Plant damage has also been ascribed to organic peroxides, formed by the reaction of ozone and atomic oxygen with the hydrocarbons commonly existing in polluted air (Haagen-Smit, Darley, *et al.*, 1952).

The basic technique of kinetic colorimetry for the determination of microgram quantities of peroxides was developed several years ago (Saltzman and Gilbert, 1959). These workers distinguished between hydrogen peroxide and peracetic acid by using neutral potassium iodide reagent.

Indeed, experimentation on the kinetics of the oxidation, by microgram concentrations of specific peroxides, of the colorless ion to the colored species is relatively scarce. However, application of this technique to help define the wide spectrum of oxidants existing in the atmosphere is appropriate.

In this present work, a variety of oxidants were chosen which have been reported as products in the photooxidation of model smog systems. A colorimetric reagent appropriate for each oxidant studied was selected, so as to produce a slowly developed color. Reagents included in this investigation are a recently developed molybdate-catalyzed potassium iodide reagent and a novel modification of the ferrous thiocyanate reagent (Cohen, Purcell, *et al.*, 1967).

Experimental

The reagents and chemicals employed in this study have been discussed in a previous paper (Cohen, Purcell, *et al.*, 1967).

Procedure. In each instance, about 12 μg. of active oxygen (O_2^-) were transferred by pipet (for liquid-phase samples) or sampled with a fritted bubbler (for vapor concentrations) into 10 ml. of colorimetric reagent. (At this point, when the potassium iodide reagent was used, the effect of the molybdate catalyst was observed by the addition of 1.0 ml. immediately after sampling.) The mixture was kept at 27° ± 1° C. Readings on a Cary Model 14 spectrophotometer at the appropriate wavelength were begun immediately and continued until the maximum absorbance occurred.

Results and Discussion

The method of kinetic colorimetry was applied to a study of the "slow oxidant." With buffered neutral potassium iodide, ozone and peracetic acid give the maximum absorbance virtually instantaneously. Hydrogen peroxide and alkyl hydroperoxides exhibit much slower color development. With molybdate-catalyzed potassium iodide, hydrogen peroxide gives an immediate absorption maximum; but the alkyl hydroperoxides still behave like slow oxidant.

A graphical method was used to identify and estimate the concentration of peroxidic compounds by making use of their kinetic rate constants for formation of the triodide complex. The method was employed for liquid-phase and vapor dilutions of hydrogen peroxide, ethyl hydroperoxide, *n*-butyl hydroperoxide, *tert*-butyl hydroperoxide, and various photochemically produced slow oxidants—e.g., from ultraviolet irradiations of aldehyde–air mixtures; the neutral and catalyzed iodide reagents were used.

A plot of the log of the undeveloped absorbance ($A_\infty - A$) *vs.* time (minutes) for a single-component system gave the characteristic straight line of a pseudo-first-order reaction (Figure 1). The half life, from which the rate constant may be calculated, was determined graphically for each oxidant tested. With neutral potassium iodide, the half lives were 14, 50, and 58 minutes, respectively, for hydrogen peroxide, ethyl hydroperoxide, and *n*-butyl hydroperoxide.

With catalyzed KI there was one striking difference. Hydrogen peroxide gave an immediate reading with no further color development, whereas the half life of ethyl hydroperoxide was 50 minutes. For *n*-butyl hydroperoxide, the half life was 52 minutes. The extinction coefficients were somewhat higher in each case.

A plot of these pseudo-first-order rate constants for the reactions with netural KI reagent *vs.* the molecular weight of the alkyl group indicates that the effect of lengthening the R-group is to decrease the rate of cleavage of the peroxygen bond. This effect becomes minimal at a chain length of four carbon

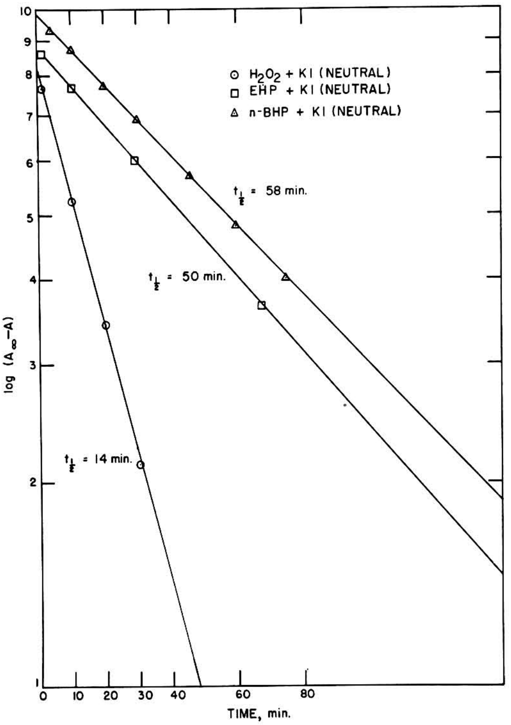

Figure 1. Kinetic colorimetry using neutral potassium iodide reagent

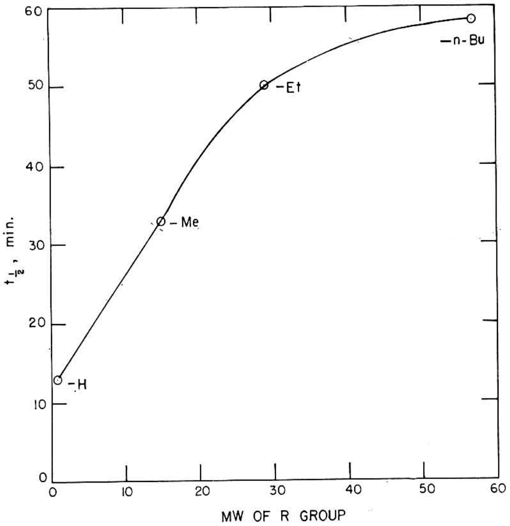

Figure 2. Effect of alkyl group on colorimetric rate constant

atoms (Figure 2). The half life of the *tert*-butyl hydroperoxide–KI reaction is around several hundred minutes (Cadle and Huff, 1950). The reaction mechanism in question may be different when R is branched.

Photooxidation of propionaldehyde at low partial pressures gave rise to a slow oxidant, which was identified by gas chromatography and kinetic colorimetry as ethyl hydroperoxide (Altshuller, Cohen, *et al.*, 1966). Similarly, photooxidation of low partial pressures of acetaldehyde produced a slow oxidant with a colorimetric half life of 34 minutes for the reaction with neutral KI reagent. This value agrees very well with the literature value of 33 minutes for methyl hydroperoxide (Figure 2), a value determined titrimetrically (Cadle and Huff, 1950).

Vapor dilutions of PAN-type compounds in the parts per million concentration range gave slow color development with the modified Griess, potassium iodide, and ferrous thiocyanate reagents. Whether this is caused by the PAN compound or by the decomposition products is not known.

In investigation of the possible use of kinetic colorimetry for the analysis of PAN compounds, the reagent chosen was the previously described ferrous thiocyanate reagent. (A plot of the logarithm of the undeveloped absorbance *vs.* time in minutes indicated a pseudo-first-order reaction, Figure 3.) A sample of the PAN compound, stored in a Teflon FEP bag, was bubbled through 10 ml. of ferrous ammonium sulfate reagent. Spectrophotometric readings at 480 mμ were begun immediately after 2 ml. of ammonium thiocyanate were added to develop the color. Readings were continued until the absorption maximum was reached. The half lives for the color development reaction were 73 minutes for peroxyacetyl nitrate and 115 minutes for peroxypropionyl nitrate. Nitrogen dioxide, sampled through ferrous thiocyanate reagent at parts per million concentrations, exhibits slow color development. The half life for this colorimetric system is 22 minutes.

Acetyl peroxide, reported by McDowell and Sifniades (1963) as an oxidant product in the photochemical oxidation of acetaldehyde in the millimeter partial pressure range, was also investigated by kinetic colorimetry. Concentrations of

Table I. Kinetic Half Times

	Half Time, Minutes for Color Development		
Oxidants	$Fe(NH_4)_2(SO_4)_2$, NH_4SCN	KI (neut.)	KI (cat.)
Ozone	0	0	0
Peracetic acid	0	0	0
H_2O_2	0	14	0
Acetyl peroxide	4.25	17	34
Methyl hydroperoxide	0	33[a]	—
Ethyl hydroperoxide	0	50	50
n-Butyl hydroperoxide	0	58	52
tert-Butyl hydroperoxide	0	>300[a]	—
NO_x	22	—	—
PAN	72.5	—	—
PPN	115	—	—
Acetaldehyde photo-oxidation product	0	34	—

[a] Cadle and Huff, 1950.

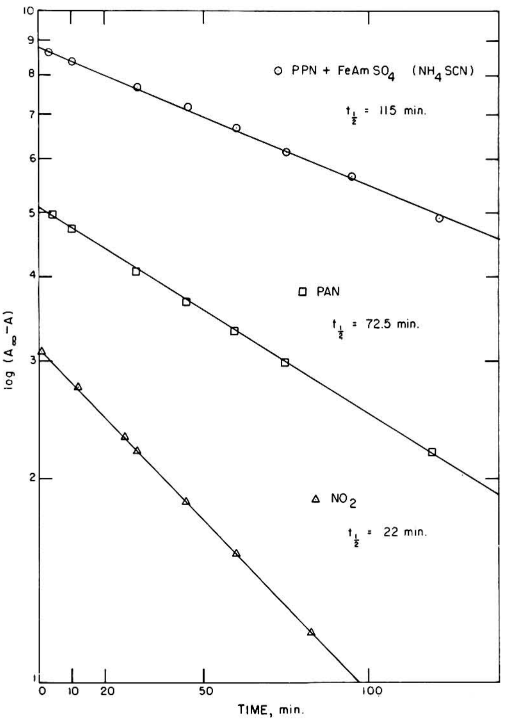

Figure 3. Kinetic colorimetry using ferrous thiocyanate reagent

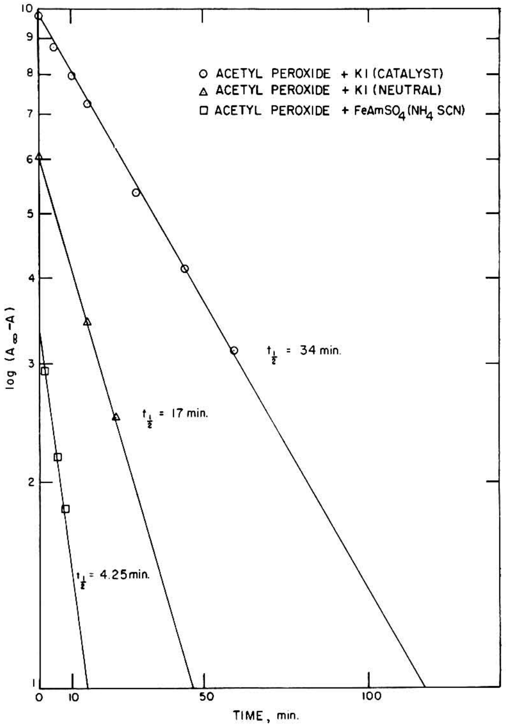

Figure 4. Kinetic colorimetry of acetyl peroxide

acetyl peroxide in the parts per million range cause slow color development with the potassium iodide and ferrous thiocyanate reagents. A plot of undeveloped absorbance *vs.* time indicated a first-order reaction with all three reagents (Figure 4). The half lives for color development with catalyzed KI, neutral KI, and ferrous thiocyanate were 34, 17, and 4.25 minutes, respectively. It has not yet been determined whether the first-order rate exhibited is attributable to the reaction of acetyl peroxide with colorimetric reagent or to the first-order hydrolysis of acetyl peroxide to peracetic acid and hydrogen peroxide products (Ross and Fineman, 1951).

Conclusions

Neutral potassium iodide showed immediate response with ozone and peracetic acid and slow color development with the other peroxides tested. Molybdate-catalyzed KI gave immediate response with hydrogen peroxide along with ozone and peracetic acid. Acetyl peroxide, nitrogen dioxide, and PAN compounds produced slow color development with the ferrous thiocyanate reagent, each at its own specific rate (Table I).

The limitations of the kinetic colorimetric method in its application to hydroperoxides are related to the structure of the alkyl group. Methyl hydroperoxide can be distinguished from higher-molecular-weight hydroperoxides, but the data indicate that ethyl and *n*-butyl are very similar in their kinetic responses and thus may be difficult to resolve. The higher homologs would presumably be indistinguishable from one another. Too, chain branching in the alkyl group can play a major role in the kinetics.

These various single-component peroxygen compounds undergo a pseudo-first-order reaction profile, exhibiting straight-line plots with characteristic slopes. Ideally, mixtures of many of these compounds in various combinations should be analyzed readily by resolving the various changes in slope into a series of linear plots, one for each component present.

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Infrared Analysis of Gases: A New Method

Mark M. Rochkind
Bell Telephone Laboratories, Murray Hill, N. J.

■ A sensitive method for infrared chemical analysis based on a cryogenic sampling technique has been proposed. Diluted gas mixtures are deposited in pulses onto a cooled alkali halide substrate; sample preparation and deposition need require only seconds. Extraordinarily simple spectra superbly suited for digital analysis result. Computer analysis of the raw spectral data suggests applications in the areas of air pollution control and atmospheric research. Spectral data for hundreds of gases might be stored within a central computer linked via telephone to numerous experimental stations. Transmitted data could be analyzed in seconds and a report communicated to a local station within minutes. Modifications of the sampling technique to accommodate liquids and solids seem possible.

Whereas low temperature optical spectroscopy has found widespread use as a research tool, no application of cryogenic sampling as an instrument for chemical analysis has been demonstrated. The recent advances in cryogenic technology which have made Joule-Thomsen refrigerators commercially available provide impetus in the area of low temperature research and bring cryogenics within the reach of most chemical laboratories. This being the case, exploitation of low temperature techniques for spectrochemical analysis is warranted.

We have developed a new method for infrared chemical analysis of gas mixtures which involves an atypical method of cryogenic sampling which is highly selective, highly sensitive, and rapidly executed, yet which requires only conventional infrared instrumentation (Rochkind, 1967). This method provides the most sensitive means of infrared gas analysis demonstrated to date. Micromole quantities of most chemical species are sufficient for positive qualitative identifications, and in many instances fractions of a micromole suffice. The method is suitable for impurity analysis. It provides a means of spectrochemical analysis for all gaseous species excepting homonuclear diatomic molecules, and modifications of the sampling procedure to encompass liquids and solids are being studied. In addition to providing a sensitive means for differentiating among structurally similar molecules, the method is capable of differentiating among isotopic species of relatively light polyatomic molecules. In range of application the proposed method is most comparable to mass spectrometry. Although its sensitivity is not so great, analysis of infrared data is considerably simpler than the multidimensional analysis required for interpretation of mass spectra. Capital investment provides another contrast; it proves sizably greater for a mass spectrometric laboratory.

Feasibility experiments recently conducted have demonstrated application of this infrared method for a series of 13 structurally similar, simple (C_1 to C_4) hydrocarbons (Rochkind, 1967). We are currently expanding our experimentation to larger hydrocarbons and molecules of more varied atomic composition. Our choice to demonstrate feasibility via analysis of simple hydrocarbons was motivated by the relatively small extinction coefficients and great similarities in normal vibrations exhibited by members of this series. Thus, success with an unadvantageous system assures credibility for the method. Although serious efforts have not yet been made to define the technique's quantitative capabilities, preliminary results indicate that quantitative methods employing cryogenic sampling can be developed.

The merit of the proposed method derives in large part from the extraordinary spectral simplifications which result from low temperature sampling. Removal of rotational degrees of freedom yields a great enhancement of spectral intensity as bandwidths are reduced from 100 to 3 or 4 cm.$^{-1}$; interspersing inert molecules in the condensed solid partially to surround and thus separate molecules of gas mixture being analyzed reduces molecular interactions to yield vibrational spectra characterized by narrow lines, well defined frequencies, and high reproducibility. Such would not be the case for spectra of simply condensed reagent gas mixtures.

Workers in the field of molecular spectroscopy will recognize the proposed technique as an adaptation of the matrix isolation method which was developed to provide controlled environments for the *in situ* generation and trapping of unstable radical species. To achieve good "matrix isolation" a reagent gas is dissolved in very high dilution in an inert gas and the resulting solution is slowly condensed onto a cooled substrate. The expectation that high dilution coupled with slow deposition will yield an inert matrix within which are dispersed randomly distributed reagent molecules is well borne out. While it is a very powerful spectroscopic technique, the matrix isolation method is time-consuming and thus not suitable for chemical analysis. Our adaptation employs an inert matrix gas but a very rapid, pulselike deposition which proves a reproducible manner of sample preparation and provides a degree of "isolation" sufficient to suppress frequency shifts which might result from interactions between reagent molecules, though not sufficient to yield the extremely narrow (1-cm.$^{-1}$ half width) bandwidths characteristic of good matrix isolation. Nonetheless, the resulting bandwidths are sufficiently narrow to permit resolution of vibrational frequencies adjacent to within a few wavenumbers.

Because the vibrational bands are well defined and because normal modes are highly sensitive to even small variations in molecular structure, the infrared identity of a single chemical species may be completely characterized by only two or three fundamentals suitably chosen from its spectrum. It is thus a simple matter to compile a compact table of "selected frequencies" describing the infrared identities of any number of gases. The high specificity of normal vibrations makes accidental degeneracies on the binary and ternary levels upon which an analysis is conducted highly improbable. Furthermore, relative intensity data (independent of experimental configuration) are available for a two-dimensional analysis.

Procedure

The actual experimental procedure is simple. Reagent gas is well mixed with a 100-fold mole excess of nitrogen; the resulting solution is deposited in ~0.5-mmole pulses onto an alkali halide substrate cooled to 20° K. The crystalline film which results is transparent and highly transmitting throughout the infrared spectral range. Whereas eight aliquots of gas mixture (~40 μmoles of reagent) are generally deposited when recording the standard spectrum of a reagent gas, as many as 48 aliquots of a synthetic seven-component mixture have been deposited without any significant loss in signal-noise due to infrared scattering. While absolute intensities will depend very strongly on the geometrical properties of the cryostat assembly, frequency reproducibility should be preserved independent of experimental configuration. Thus, standard spectra (frequencies, relative intensities, bandwidths) for gaseous chemical species need be recorded only once to be permanently cataloged.

The proposed method of infrared analysis is amenable to extensive automation. A manifold system equipped with high vacuum solenoid valves, for example, is easily fabricated to provide an automated system for gas expansion, dilution, and pulse deposition. More exciting, however, is the clear application of digital control to analysis of the raw spectral data. Such an approach is encouraged by the high frequency reproducibility of the technique and the well defined spectral bands. A digital computer can compare and match a raw spectrum with a table of "selected frequencies," even one containing data on hundreds of distinct chemical species, in a matter of seconds. In fact, a digitally controlled analysis might at no further expense be carried out on a two-dimensionsal level—i.e., involving relative intensities in addition to frequencies—to ensure against accidental degeneracies.

Master File

Because infrared spectra are readily digitized, it is optimum to keep a master file of selected frequencies within some centrally located computer and to perform all analyses via data transmission to this central facility. This is an eminently practical scheme, for it relieves the experimental station of amassing "selected frequency" data, of training personnel in the interpretation of raw spectra, of developing and maintaining computer software to execute analyses, and of the economic strain in supporting a reasonably sophisticated computer facility. With the degree of automation to which the sampling procedure admits, analyses of complicated mixtures might be effectively carried out by nonprofessional technical personnel.

The telephone provides a method of data transmission which is straightforward and surprisingly economical. It is inexpensive to record digital spectra on perforated paper tape. Spectra may then be transmitted via Bell System Data-Sets over normal telephone lines at no premium charge. A 3-minute transmission which could involve the transfer of as many as 216,000 bits of information would incur costs at the same rate as a 3-minute voice conversation. Thus spectral data can be transmitted between any two points in the country at strictly nominal cost. Transmission of 2000 distinct spectral measurements would require from 2 to 5 minutes of transmission time, depending on the detailed peripheral equipment; and the required capital investment in suitably flexible peripheral equipment is small. A single computer facility should be capable of handling more than 1500 sets of spectral data per 24-hour period. As raw spectra are received from various experimental stations, they might be queued on a magnetic disk file and as the analyses were completed the results could be voice-telephoned or teletyped back to the station of origin using the same Data-Set facility employed to transmit the raw spectra. Alternatively, or in addition, a record of the analysis might be prepared for mailing by auxiliary digital output equipment without human participation. Standard spectra of new chemical species could continually update the master file without revision of the analysis programs. Thus a single perpetuating master file would be retained, copies of which could be provided to affiliated centers.

Applications

The suggested scheme for digitally controlled analyses of spectral data coupled with a practical means of data transmission greatly extends the range of application for the proposed method of analysis. In addition to general use in the research laboratory, for example, where the chief virtue of the method is that nothing need be known about the contents of a gas mixture prior to analysis, there are very real applications in the field of air pollution control, in the general area of airborne atmospheric research, and in the chemical process industry where methods for impurity analysis are invoked as means of quality control.

In the field of air pollution control the automated infrared method permits marked standardization in determining the pollutant composition of exhaust gases. For example, inexpensive, evacuated polycarbonate bulbs (100-cc. volume) fitted with some break-seal device might be provided for sampling effluent gases where the pollutant composition of such gases was in question or where adherence to a pollution code needed to be demonstrated. An unbreakable plastic bulb could be simply capped, after disrupting the vacuum in an effluent stream, and mailed to a local experimental station where a spectrum would be digitally recorded and transmitted via telephone to some central computer facility. The computer would perform the analysis, record the results in its library for future reference or to ensure corrective action, and initiate a certified report on the analysis to the local station. This proposal seems thorough and economically and practically more sound than the construction and support of completely self-contained local analytical stations throughout the country. That there is a need for some kind of analytical network in the area of air pollution control is beyond question. Whether infrared spectroscopy provides the right compromise between analytical sensitivity and cost is something which should be carefully explored. What is certain is that whatever analytical method is adopted, it must be disposed to very general analysis.

The fact that the proposed method requires no knowledge of sample composition prior to analysis suggests its use in interplanetary atmospheric research. Such an application would permit an orbiting vehicle to define the stratified composition of a planetary atmosphere through a series of sequential samplings: spectral data to be telemetered back to earth for analysis. Infrared gas phase studies, while instrumentally simpler, are difficult to interpret and are not capable of providing the kind of detailed information which repeated samplings of an actual atmosphere would yield. There is also a potential application in the field of exo-biology in the search for extraterrestrial life. In addition to analyzing natural vapors, a soft-landed package might be employed in the search for organic material via partial thermal reduction of solid matter to the gaseous state; very low vapor pressures would suffice. The use of solid sampling procedures in lunar research is being considered.

Technical details describing experimental procedures and spectrometry have been published (Rochkind, 1967).

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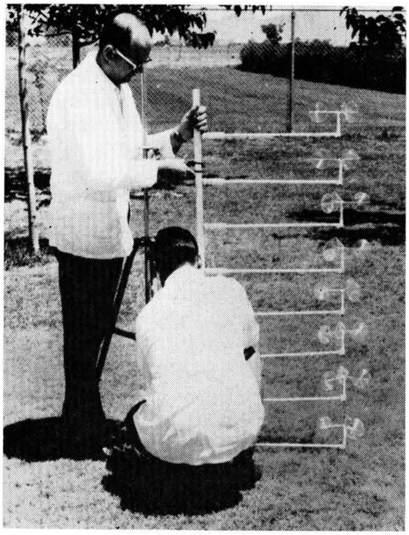
NEW PRODUCTS DIGEST



Microclimate Wind Recorder Developed

What happens with regard to air motion within the microclimate—the portion of the atmosphere that lies immediately above the surface of a field—is very important because light winds at the earth's surface cool growing plants, carry carbon dioxide to leaves for use in photosynthesis, and influence water-use efficiency of crops. The problem has been that standard anemometers do not record low enough wind speeds to be useful in microclimate studies.

Scientists in the Agricultural Research Service (U. S. Department of Agriculture) have solved this recording problem by perfecting a highly sensitive wind gage at their Water Conservation Laboratory in Phoenix, Ariz. The new gage resembles oridinary anemometers in most ways, but the cups that catch the wind are cone-shaped instead of hemispherical and are constructed of a very thin, extremely light plastic. Both shape and weight of the cones contribute to the sensitivity of the device.

The device, which is sensitive to wind speeds of less than one tenth of a mile per hour, uses a frictionless recording system. The spinning shaft of the anemometer interrupts a beam of light focused on a photoelectric cell, which relays the frequency of interruptions to an instrument that automatically calculates and records wind speed. Several of the cup assemblies (above) can be mounted one above the other to measure variations in the movement of different layers of air. Specifications are available. Please circle **60** on the Readers' Service Card.

Silylating Agent

Silyl 8, a chemical formulation for conditioning gas chromatographic columns, is injected directly into the column and acts to block active sites with an inert and stable trimethylsilyl group. It is intended for use where a highly inert column is desired and should not be used on H-bonding type phases such as glycerols, carbowax, and the like. Available in 25 ml. Hypovials (several hundred injections). Pierce Chemical Co. **61**

Continuous Dissolved Oxygen Monitor

For use in dissolved oxygen analyzers with p.p.m. or p.p.b. capabilities, the portable, remote (up to 1000 feet) sampler and probe unit has a magnetic-coupled, a.c.- or d.c.-driven, cleaner-agitator which assures minimum fouling of the membrane and provides optimum calibration stability. A large anode increases performance life between cleanings by an order of magnitude. Membranes of up to 2 mils thickness may be used without sacrifice in response rate. Weston & Stack, Inc. **62**

Calibration Device

A direct-reading conductance box, Model CD-6, for calibrating conductivity equipment provides six decade dials which permit direct reading of precise conductance units from 1 micromho to 1,111,110 micromhos. Beckman Instruments, Inc. **63**

New Analytical Services

DeBell and Richardson, Inc. has added gel permeation chromatography and thermal analysis services to its plastics research, development, engineering, and testing programs. In addition, the firm is prepared to test plastics for fungus resistance as well as other physical, mechanical, or electrical properties. R&D planning counsel is offered. DeBell & Richardson, Inc. **64**

Vertical Pump

Called the "Vane-Flo", this vertical, dry-pit, solids handling pump can pass any solid that enters its suction port. The straight centrifugal units are available in 3-, 4-, and 6-in. port sizes, with each model having swirl action created by partially recessed impellers. Capacities range to 3000 g.p.m. and total heads to 140 feet. The pump is available in cast iron, Meehanite, Ni-Resist, Ni-Hard, 28% chrome iron, and 316 stainless steel construction to suit a variety of corrosive slurry applications. ITT Marlow. **65**

Balance with Dual Readout

The Mettler P6 fully automatic, top-loading balance provides analog as well as digital (to 0.5 gram) readouts, weighs objects up to 7500 grams, handles bulky and odd-sized objects readily because it has no weighing chamber and is precise to +0.25 g. Mettler Instrument Co. **66**

Polarographic Analyzer System

Model SSP-1 single-sweep polarographic analyzer system consists of a storage oscilloscope with two polarographic plug-in units which will provide polarograms in seconds that can be stored up to one hour. An amplifier unit and a time-base unit are housed in the one console, along with display adjustment controls and calibration wheels. Chemtrix, Inc. **67**

Thin Layer Chromatography Scanner

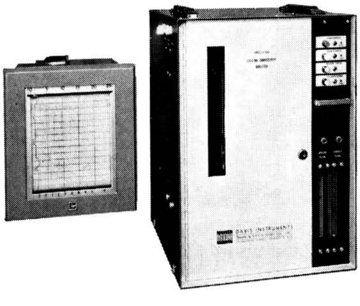
Developed primarily for the fluorometric quantitation of chemical entities separated by thin layer chromatography, the scanner has applications in the textile and paper industries, in ink and paint industries, for pesticides, and for a variety of general biochemical analyses. The instrument can measure native fluorescence, reagent induced fluorescence, or fluorescence quenching. The unit operates from 117 volts a.c. and has a scan rate of 2.4 cm. per minute. G. K. Turner Associates. **68**

5-Channel Dissolved Oxygen Analyzers

Model 88-A is suitable for continuous BOD analysis and oxygen depletion studies in the plant or lab and employs a new process which eliminates the need for Winkler tests. Model 88-B is available for sewage plant oxygen monitoring, pilot plant studies, aeration efficiency and design analysis, and like uses. The five rugged oxygen and temperature probes may be operated at any distance from the analyzer, and do not require frequent calibration because they are unusually stable. Both units record continuous data for five simultaneous tests, have a full oxygen range of 0–20 p.p.m., and are available for line or portable operation. Delta Scientific Corp. **69**

Gas Analyzer

Model MS 100 high speed r.f. mass spectrometer gas analyzer identifies gas molecules from mass 1 to mass 600. The two-console system records values as low as 100 nanograms, operates at ambient temperatures without the need for coolants, and records the output display of the mass peaks on high speed photosensitive recorder strips. Readout is linear across the band, facilitating direct identification of mass peaks. A record of the entire mass range from 1 to 600 can be produced in 1 sec. General Electric Co. **70**



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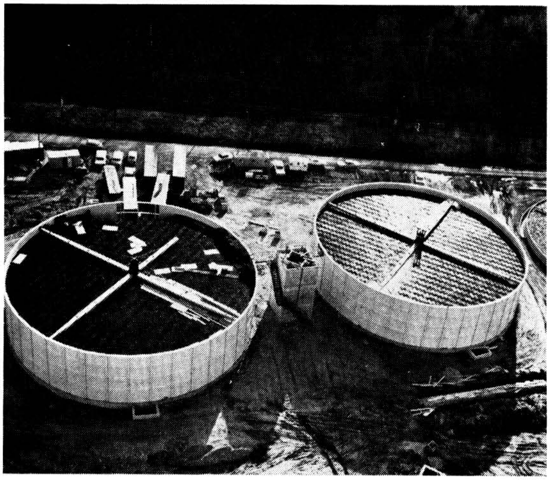


Improved Waste Facility

In 1935, when the population of Cedar Rapids, Iowa, was only 60,000, the city built a water pollution control plant which would handle a maximum of 8 m.g.d. In 1955 the treatment plant was expanded to a capacity of 18 m.g.d. As the population grew to the present level of 105,000, the city hired the firm of Howard R. Green Co., a consulting engineering firm, to study the problem of treating its municipal and industrial wastes and to design new facilities to supplement the old.

The consultants recommended increasing the capacity of the plant to 28.4 m.g.d. average flow. This entailed a $3 million construction project. Two new intermediate filter towers accounted for about 50% of the total cost of the improvement project. They are 122 feet in diameter by 21.5 feet deep, and handle an average of 25 m.g.d. They are designed to remove 61% of the 74,900 pounds per day loading of BOD that the water will carry. In operation, the two towers are equal in effectiveness to 14 of the old rock filter aerators. Three of these old filters, 135 feet in diameter by 6 feet deep, are in use along with the new filters.

Other improvements to the plant include three primary clarifiers, an intermediate clarifier, a final clarifier, and two additional sludge thickeners. The new equipment was installed alongside the old facilities and are used along with the old.

The new installations make much use of Surfpac media, manufactured by the Dow Chemical Co. The herringbone packing pattern of the individual honeycomb design blocks yields a high surface area (27 square feet per cubic foot) and high void space (94%). The towers were constructed in only 246 days.

Specifications for Surfpac media as well as for the improved plant facilities are available. Circle **71** *on the Readers' Service Card.*

Fume scrubbers. A 6-page brochure deals with fume scrubber selection, capacities and efficiencies, design, and cost. Blowers, towers, exhaust systems, tanks, and components are illustrated. Industrial Corrosion Control of Ohio, Inc. **72**

Environmental control. A 12-page bulletin describes what one company in one state is doing and has been doing for 30 years to solve its pollution problems for the benefit of society. Entitled "Air, Water, and Industry," the booklet expresses the conviction that "...pollution control is a part of the cost of doing business and we have always treated it that way. We firmly believe that industry can be clean and profitable at the same time, and we have proven this to our satisfaction." Dow Chemical Co. **73**

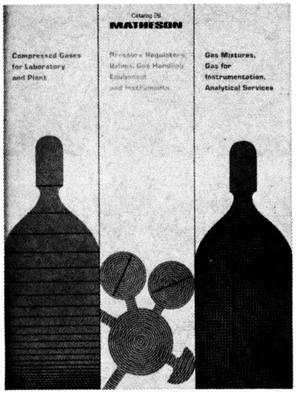
Chemical catalog. A biochemicals catalog covering amino acids and peptide reagents, rare carbohydrates, enzyme substrates, lipids, steroids, and bioanalytical reagents is available. The 99-page catalog features special sections on venoms, silylation reagents, and GLC standards. Pierce Chemical Co. **74**

Water management. An 8-page bulletin outlines the scope of water management services available by Calgon, from water source through all phases of plant usage to possible waste water reclamation and reuse. Calgon Corp. **75**

Industrial turbine flowmeter. A 4-page specification describes a turbine flowmeter for industrial use. Either sleeve or ball bearings may be used interchangeably without affecting metering accuracy. Fischer & Porter Co. **76**

Consulting service for Industry. A 12-page brochure outlines the ways in which a consulting service can help to find a workable and economical solution to a plant's pollution emission problems, both air and water. Chemico Consulting Division. **77**

Low-conductivity magnetic flowmeter. A fact sheet describes an obstructionless magnetic flowmeter for liquids with specific conductivities one tenth that of distilled water. Fischer & Porter Co. **78**



Gas chromatography accessories catalog. A 35-page accessories catalog presents a wide range of column materials and gas chromatograph accessories as well as listings of most of the liquid phases and solid supports in common usage in the field. Varian Aerograph. **79**

Testing services. Three checklists outline the types of services applicable to problems of air and water pollution and solid waste disposal. These include chemical and instrumental analyses, stack sampling, source emission studies, evaluation of pollution abatement equipment, corrosion studies, waste utilization, and monitoring services. York Research Corp. **80**

Galvanic cell oxygen analyzer. Bulletin 638 describes a compact 7½ lb. portable galvanic cell oxygen analyzer that generates its own operating current. The unit reads dissolved oxygen to ±0.1 p.p.m. in less than 1 minute, may be used for continuous monitoring, is unaffected by 50 lb. or more hydrostatic pressure, and has an indicating meter. Precision Scientific Co. **81**

Instruments catalog. An 82-page catalog contains complete specifications for modular nuclear instruments and a guide to assist the user in selecting the proper combination of modules for a specific application. A section describes input and output accessories. Nuclear-Chicago Corp. **82**

Maps of Atlantic coast. A series of 15 bathymetric maps of the 400-mile stretch of seabed from Massachusetts to Maryland has been released by the U. S. Department of Commerce's Coast and Geodetic Survey service. Produced at a scale of 1:125,000, the maps are sold for 40 cents each. Coast and Geodetic Survey. **83**

Microcoulomb recorder. A fact sheet provides complete information on the Model 725-21 monitoring instrument for free chlorine, iodine, fluorine, and ozone in the parts-per-hundred-million range. The meter and companion strip chart recorder feature continuous readout in microamperes linearly proportioned to the oxidant content of the gas sampled. Mast Development Co. **84**

Precision humidity measurement and control. A list of reprints on various aspects of hygrometry should be of interest to those interested in knowing about relative humidity or in determining hygrometer instrumentation required for measuring and controlling humidity. Hygrodynamics, Inc. **85**

Reversible counter. A 44-page book, *Using a Reversible Counter*, surveys some of the applications for reversible counters. These counters measure differences between their two inputs, as well as sums of the inputs. Transducers covered in the book include laser interferometers, optical gratings, tachometers, and several types of flowmeters. Hewlett-Packard. **86**

Water treatment folder. A folder on water treatment and pollution control explains continuous ion exchange as a process for water softening, demineralization, and iron, phosphate, nitrate, or fluoride removal. Chemical Separations Corp. **87**

Sulfide ion activity electrode. A fact sheet is available on the direct measurement of sulfide ion by an electrode which can be used over the full pH range 0-14. Orion Research, Inc. **88**

Filter underdrain system. A fact sheet about a new filter underdrain system called Roto-Scour details the advantages of the system, which has its greatest advantages where turbidity load to the filter is high or where high filtration rates are employed. Graver Water Conditioning Co. **89**

Quarterly AutoAnalyzer newsletter. A new periodical, *Trends: Automation in Analytical Chemistry*, is oriented toward the AutoAnalyzer user, will cover clinical methods, enzyme assays, immunology and hematology, pharmaceutical research, agricultural chemistry, pollution abatement, and other industrial analyses. The newsletter will be sent on a regular basis, free of charge, upon request. Technicon Instruments Corp. **90**

Instruments catalog. A 44-page catalog features equipment for immunoelectrophoresis and immunodiffusion, thin layer electrophoresis, electrodialysis, and cytology. Air sampling accessories and radiation monitors are included in the catalog. Gelman Instrument Co. **91**

Silylation bibliography. A 12-page booklet, *A Bibliography of Silylation: Synthetic Methods and Analytical Uses*, is indexed by subject and author and contains 309 references. Pierce Chemical Co. **92**

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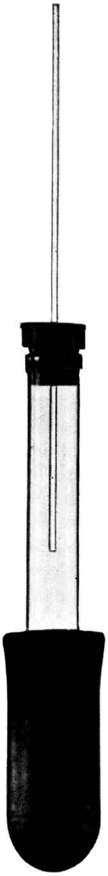

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BOOKSHELF

An Ecological Handbook: A Gaggle of Facts

Environmental Biology. Compiled and edited by Philip A. Altman and Dorothy S. Dittmer. xxi + 694 pages. Federation of American Societies for Experimental Biology, Bethesda, Md. 20014. 1966. $15.00, hard cover. *Daniel J. Nelson is in the Radiation Ecology Section, Health Physics Division of the Oak Ridge National Laboratories, Oak Ridge, Tenn.* 37830.

By Daniel J. Nelson

"Environmental Biology" is the fourth book in the series of handbooks of biological data compiled for reference purposes under the auspices of the Federation of American Societies for Experimental Biology. The book follows the previously established format and consists of tabular data prepared by specialists in zoology, botany, and medicine. The handbook is an ambitious attempt to categorize the responses of living systems to environmental conditions. The following environmental factors are considered in the 10 separate sections: temperature; radiant energy; sound, vibration, and impact; acceleration and gravity; atmosphere and pollutants; atmospheric pressures; gases; water; solutes; and biological rhythms. Two appendices are included which give cross references for scientific and common names of organisms. In addition there is a thorough index.

The editors have done an admirable job in organizing the data from approximately 450 contributors. Data are presented in 190 tables with the contributors and references listed immediately following each table. Hence, the handbook can serve as a convenient reference source for selected environmental factors. The scope of an environmental handbook, however, should generally be restricted to environmental factors. The editors attempted to include data on normal biological experience as well as changes that have occurred in the environment as the result of human cultural activities. On this basis I think most ecologists will be curious about the inclusion of some types of specialized data such as the responses of individual astronauts and cosmonauts to weightlessness. In fact, the whole section on acceleration and gravity is devoted to the specialized field of aerospace medicine. Similarly, data on the effects of underwater explosions on man and other mammals or the chemical composition of the atmosphere of nuclear submarines appear to be directed toward a highly selected audience or the idle curiosity of others.

Much of the material included would be useful for industrial hygienists—such as the data on responses to radio-frequency radiation, effects of exposure to noises, and the effects of breathing unusual gaseous atmospheres. Food technologists can find the thermal death point for nonpathogenic bacteria in chopped okra and a variety of other foods. I am sure that other technical disciplines will find similar information of value.

Atmospheric environment

The three sections (about 30%) of the book devoted to various aspects of gaseous environments result in very comprehensive coverage of this portion of the environment. Atmospheric pollutants are considered specifically with respect to sources. And data on the effects of the various pollutants on animals and plants are included. Interestingly, the effects of abnormal carbon dioxide concentrations on the various body functions of mammals require nearly 45 pages, while the secular change in the carbon dioxide content of the atmosphere is indicated weakly in a footnote.

A relatively good summary of the effects of temperature on a wide variety of organisms is included.

The sections on water and solutes provide much data on interactions among soil, water, and plants. Data on the responses of aquatic organisms to water quality are restricted to the effects of salinity. With the volume of published research on toxicities of metallic ions, pesticides, and organic compounds to fish and other aquatic life, a table of toxicities would have been desirable. Water quality affects the toxicity of various pollutant materials, which might explain a reluctance of the editors to include the data. However, as potential users of the handbook should note, many of the tables contain an explanatory heading which discusses constraints that are to be considered in applying the data.

Missing information

There are other bodies of information that could be included in the book, such as dissolved oxygen requirements for fish. Populations of organisms in nature and their characteristics (such as density, birth rate, death rate, and fecundity) are important environmental attributes, but this entire topic was excluded. Similarly, despite the concern for man-induced environmental alterations, the carefully documented levels of radioactive fallout are not mentioned nor are the levels of pesticides in the environment considered. The effects of ionizing radiation are reported for mammals, for dominant plants in major ecosystems, and for dormant seeds. The exclusion of data on other organisms has resulted in an uneven coverage of the effects of ionizing radiation.

The scientific names of organisms usually are given in the tables, along with synonyms. In the case of the apple (*Malus pumila*) the synonymy is confused among the various entries in several tables. The two appendices giving cross references for common and scientific names of biota are useful and quite complete. I had some trouble identifying the viscacha and the huallata. The llama is generally known and the vicuña has political fame. None of these species was included in the appendices.

Attempting to catalog biological systems in a handbook is a difficult task. I feel that the editors and contributors have done a remarkable job in organizing data. Obviously, the advisory committee on this handbook chose to include much material of doubtful application to natural environments. As an ecologically oriented environmental scientist, I think the title is a misnomer. However, I will use this new handbook for selected data as I have used the previously published handbooks.

Local Weather: More Order, Less Chaos

Watching for the Wind: The Seen and Unseen Influences on Local Weather. James G. Edinger. 149 pages. Doubleday & Co., New York, N.Y. 10017. 1967. $4.50, hard cover; $1.25, paper. *Laurence E. Strong is with the Department of Chemistry, Earlham College, Richmond, Ind. 47374*

By Laurence E. Strong

Dr. Edinger has written a most interesting account of some of the main factors that determine local weather. The book is intended for amateur meteorologists. Much of the description relates to weather conditions found in the Los Angeles area where the author lives. His concern is that of showing, by giving examples, the possibilities in observation, interpretation, and appreciation of one's own local weather. Publication of this book represents a joint venture by the American Meteorological Society and Educational Services, Inc. These two groups intend this book to be one of a series for high school science students and interested laymen.

The story begins with a discussion of large-scale air circulation patterns over and around the United States. Vertical motion of air and the resultant changes in pressure and temperature are described. Emphasis is given to the role played in air motion by the condensation or evaporation of water.

Since the author is interested in presenting weather watching as an interesting activity for the amateur at home, he devotes considerable attention to the effects of local terrain on air movement. His illustrative examples are drawn mostly from the interaction of air masses, water masses, and land masses along the Pacific Coast of southern California. In some detail he shows how much of the Los Angeles weather flows from a large anticyclone off the California coast.

Smog is the subject of one chapter. The author shows how local weather conditions favor smog formation. At the same time he argues that weather modification, even if possible, cannot provide a way of improving the situation. Along with smog, fire hazards peculiar to California weather are discussed.

Probably the most interesting chapter is entitled "A Meteorology Field Trip." It recounts a 500-mile auto trip from Monterey Bay south to Los Angeles. The author's purpose is to show the variety of observations and interpretations that can be made of wind and weather from the visual data available to anyone who cares to look. The purpose is well served by this concluding chapter.

Force or energy

As a book for young students of science there are a few points to question. Modern science textbook writing tends toward the use of the MKS system for quantitative data. However, in this book the British system is used for no readily apparent reason. Somewhat more dubious is the author's statement (page 50) "Air does not occur as separate bits and pieces, like billiard balls or Chevrolets. Instead, air is continuous and extremely deformable." However, students brought up on a molecular theory of gases may find this treatment of air as a fluid rather at odds with their own developing notions. The author discusses the motion of air masses in terms of forces. However, it seems to me that the treatment would be simpler and more in line with modern high school physics courses if energy, not force, were the guiding principle. It would then be feasible to discuss the gravitational potential energy of an air mass and how changes in this potential energy would be accompanied by temperature changes, phase changes, and interaction with land masses and other air masses.

The author wrote "Watching for the Wind" in hopes he would help people to see "a little more order, a little less chaos, in the seemingly random distribution of the clouds, wind, rain, and snow that together make up the local weather." He has succeeded admirably in fulfilling his hopes. Readers young and old will find the book well worth their time and money.

LETTERS

More on Lake Erie

DEAR SIR:

Your feature article in the March (page 212) issue on Lake Erie pollution, reviews this problem but fails to bring forth certain facts which I believe focus on the real situation in this lake.

The facts to which I refer are the following:

1. The oxygen depletion within the hypolimnion of the central basin was found, in 1964, to cover an area of 2600 square miles. The oxygen concentration in the bottom 6 to 10 feet of water was seldom above 2 mg./liter. When we convert these dimensions into oxygen deficit, at least 2.7×10^8 pounds of oxygen deficit existed at that time.
2. By using the population of the Lake Erie watershed and by applying certain factors based upon existing treatment facilities, we calculate the annual oxygen demand of the wastes draining into the watershed to be 1.8×10^8 pounds.
3. Since the *annual* input of oxygen demanding wastes to the drainage basin is less than the oxygen deficit found in the central basin of Lake Erie, a deficit which developed in a period of a few weeks, obviously a source of oxygen demand exists that is much larger than the total oxygen demanding discharges from the population of the basin.
4. The only other source that could create such a large deficit would be "natural" and would be based on nutrient effects. For Lake Erie, as well as the other Great Lakes, phosphate is the critical nutrient controlling the productivity of these waters.
5. A daily net fallout of phosphate into Lake Erie is 150,000 pounds which, on an annual basis, calculates to be 5.5×10^7 pounds PO_4.
6. By use of the familiar ratio of 100 C: 16 N: 1 P, for natural organic matter, the above quantity of phosphate is capable of generating 1.8×10^9 pounds of organic carbon which, upon decay, would create an oxygen demand of 4.9×10^9 pounds of oxygen.
7. This is 27 times the quantity of the oxygen deficit found in the lake in 1964. What is even more important, this "natural" oxygen demanding load probably occurs in pulses during the warmer seasons, making its effect on the lake much greater than if it were to occur continuously throughout the year.

I hope these facts will dispel the premise that no cause and effect relationship exists or that there is no solution to the oxygen deficit problem. If the recommendations of the Federal Conference on Lake Erie with reference to phosphate removal from effluents are carried out, the resulting reduction of phosphate inputs should show an immediate improvement in the oxygen deficit situation.

The source of the data used in the above calculations was the "Report on Pollution of Lake Erie and Its Tributaries, Part I" (dated July 1965) and presented at the Federal Conference on Lake Erie Pollution held in August 1965, in Cleveland and Buffalo.

The subsequent calculations from this data source were presented before the Natural Resources and Power Subcommittee of the House Committee on Government Operations, at Syracuse, N. Y., Aug. 19, 1966, by Mr. William Q. Kehr of the Federal Water Pollution Control Administration, my colleague at that time.

S. Megregian

Director of Research
Metropolitan Sanitary District
of Greater Chicago, Ill.

Editor's Note: The feature article, "Lake Erie—Dead But Not Dying," was based largely on a paper given by Moffett, Carr, and Kemp at the AIChE meeting in Detroit late last year. The "Report on Pollution of Lake Erie and Its Tributaries (Part I)" to which Mr. Megregian refers was published in July 1965 by HEW's Public Health Service, Division of Water Supply and Pollution Control.

Foam Separation—An Additional Look

DEAR SIR:

I fear some readers may infer that the general subject of foam separation is circumscribed by its description in the article on foam separation that appeared in the February issue (page 116) of ES&T. Accordingly, I think it worthwhile to point out some additional aspects.

The article describes only the simple mode of operation; i.e., where feed enters the liquid pool. However, as with many other methods of separation, foam separation columns can also be operated in other modes (Fanlo and Lemlich, 1965). For example, in the stripping mode, feed is injected some distance above the pool and trickles down through the rising foam. The resulting countercurrent stripping action further purifies the bottoms. In the enriching mode, some collapsed foam drains back down the column to serve as reflux. This further enriches the foam overflow. In the combined mode, both stripping and enriching are employed. For certain situations these other modes offer considerable advantage over the simple mode.

It is also worth noting that foam separation can be applied to various surface inactive solutes including certain metallic ions by first adding a suitable surfactant to unite with them and/or adsorb them at the surface of the bubbles (Rubin and Gaden, 1962; Sebba, 1962; Banfield, et. al., 1965). This can sometimes be accomplished quite selectively. Thus the potentialities of foam separation are quite broad and are not necessarily limited by an initial lack of surface activity.

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Banfield, D. L., Newson, I. H., Alder, P. J., *Am. Inst. Chem. Engrs.-Inst. Chem. Engrs. Joint Symp.* Preprint 1.1, Inst. Chem. Engrs., London, 1965.

R. Lemlich

Professor of Chemical Engineering
Cincinnati, Ohio

MEETING GUIDE

June 1–2
Vanderbilt University School of Engineering

Sanitary and Water Resources Engineering Conference

Noel Hotel, Nashville, Tenn.

In addition to sessions on water resources engineering, design and operation of treatment processes for municipal and industrial wastes, and hydraulic and hydrologic aspects of waste water collection and disposal systems, a special session will be devoted to atmospheric pollution and control.

June 4–9
American Water Works Association

87th Annual Conference

Atlantic City, N.J.

Sessions on water resources will focus on federal and state action to develop programs to ensure an adequate water supply for the nation. Included will be a program on the Grand Canal Project to divert seven Canadian rivers into the Great Lakes and the Long Island Dam Project to dam both ends of Long Island Sound to make it into a fresh-water reservoir.

June 11–16
Air Pollution Control Association

60th Annual Meeting

Sheraton-Cleveland Hotel, Cleveland, Ohio

Technical sessions will be directed at such things as air pollution and the professional chemist, long-lived pollutants, experimental exposures, personnel and training, air quality control, equipment, solid wastes, meteorology, and odor.

June 11–16
National Research Council (Division of Biology and Agriculture)

International Symposium on Eutrophication

University of Wisconsin, Madison, Wis.

The symposium will review the status of world knowledge of the problems of eutrophication, the aging of lakes and streams brought about by natural or man-induced forces. Invited papers will be presented by 36 international specialists in the fields of botany, chemistry, limnology, zoology, hydrology, and sanitary and agricultural engineering. The meeting will serve as a forum for an exchange of views on the problems and will include discussions of public policy and the broad social and economic consequences of eutrophication. At the conclusion of the meeting an executive session will be convened to prepare recommendations for action.

June 12–16; 26–30
Manhattan College, Federal Water Pollution Control Administration

Twelfth Summer Institute in Water Pollution Control

Manhattan College, New York (Bronx), N.Y.

The institute is divided into three courses: Stream and estuarine analysis, June 12–16; Physical and chemical waste treatment, June 12–16; and Biological waste treatment, June 26–30. Fee for each course is $150, but stipends and travel allowances are available for qualifying U.S. citizens. Write: Donald J. O'Connor, Civil Engineering Department, Manhattan College, New York, N.Y. 10471.

June 15–16
U.S. Departments of Agriculture and Housing and Urban Development

Soil, Water, and Suburbia

Jefferson Auditorium, Department of Agriculture, Washington, D.C.

In a conference called on the general subject of land and water management in suburbia, the two sponsoring groups will join with land developers, investors, planners, architects, engineers, scientists, and county and municipal leaders to seek solutions to problems created by suburban land development. Specifically, the conference will cover all major phases of soil and water management in connection with land development, provide practical information for planners and developers, determine needs for additional research, and improve communication with developers and others concerned with rural-fringe areas.

June 21–30
University of California, Berkeley

Combustion-Generated Air Pollution

Berkeley, Calif.

Designed for professional engineers involved with problems of combustion-generated air pollution and for others in such fields as medicine, public health, and industry who are interested in fundamental knowledge and current practice, the program will be presented by invited experts from fields of engineering, chemistry, meteorology, biology, and public health. For more details: Engineering Extension, University of California, 2223 Fulton St., Berkeley, Calif. 94720.

June 27–30
American Society of Agricultural Engineers

60th Annual Meeting

University of Saskatoon, Sask., Can.

A joint meeting of the ASAE and the Canadian Society of Agricultural Engineering, the meeting will include sessions on the environment and its control for crop storage and on pesticides, their application, and their fate.

July 3–7
Gordon Research Conference on Environmental Sciences

Air Pollution: The Oxides of Nitrogen

Crystal Inn, Crystal Mountain, Wash.

The aim of the conference is to summarize what is known, discuss research in progress, and suggest further research on the subjects of production, monitoring, effects, and control of the oxides of nitrogen. As usual at Gordon Research Conferences, discussions are informal. Contact Dr. W. George Parks, director, Gordon Research Conferences, University of Rhode Island, Kingston, R.I. 02881, for registration information.

July 5–8
National Society of Professional Engineers

33rd Annual Meeting

Statler-Hilton Hotel, Hartford, Conn.

Among the various committee reports slated for presentation are papers on pollution control and water policy.

August 23–25
American Society of Civil Engineers (Sanitary Engineering Division)

National Symposium on Estuarine Pollution

Stanford University, Stanford, Calif.

Designed to satisfy the needs of sanitary engineers and scientists concerned with the effects and control of pollution in estuaries, the symposium will cover recent studies on the effects of municipal, industrial, and agricultural pollutants on water quality and aquatic life, as well as the distribution of such pollutants by tidal action, wind, sunlight, temperature, and other physical, chemical, and biological factors. Also planned are discussions on forecasting techniques, model studies, and recent developments in water quality management.

August 28–30
Environmental Engineering Intersociety Board and American Association of Professors of Sanitary Engineering
Second Conference on Environmental and Sanitary Engineering Education
Technological Institute, Northwestern University, Evanston, Ill.

Sessions will focus on the curriculums for environmental engineering students, planning of environmental engineering systems, and the criteria and mechanism for accreditation of programs in environmental engineering, among other topics.

September 10–15
American Chemical Society
154th National Meeting
Chicago, Ill.

The Division of Water, Air, and Waste Chemistry will present, in joint efforts with other divisions, discussions of scientific information resources for the water researcher; water resources; and absorption from aqueous solutions. Other programs of interest planned are **Foam Fractionation** by the Division of Industrial and Engineering Chemistry and **Microbial Waste Treatment** by the Division of Microbial Chemistry and Technology.

October 2–6
National Institutes of Health
17th Annual Instrument Symposium and Research Equipment Exhibit
National Institutes of Health, Bethesda, Md.

The instrument symposium will include discussions of holography, laboratory computer usage, ultramicroanalytical techniques, new frontiers in spectroscopy, thermoanalytical methods, low temperature luminescence, and molecular separation by size and charge. The exhibit (which ends Oct. 5) will include examples of the latest types of research equipment available from instrument manufacturers.

October 8–13 and 15–18
Water Pollution Control Federation
40th Annual Conference
Hotel Americana, New York, N.Y. (Oct. 8–13)
Puerto Rico Sheraton Hotel, San Juan, Puerto Rico (Oct. 15–18)

The meeting will be held in two sessions. The first will take place in New York City from October 8–13; the meeting will reconvene in San Juan, Puerto Rico, from October 15–18. The New York sessions will be on water quality standards, industrial wastewater research, estuary problems, nutrient removal, and like topics. The Puerto Rico sessions will be concerned with refinery waste treatment, refinery wastes effect on marine biology, open-pit mines, wastes, rum distillery wastes, and other problems.

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