



ENVIRONMENTAL Science & Technology

Emphasizing

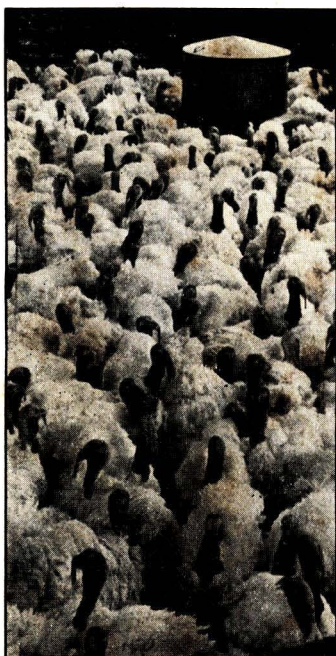
Water,

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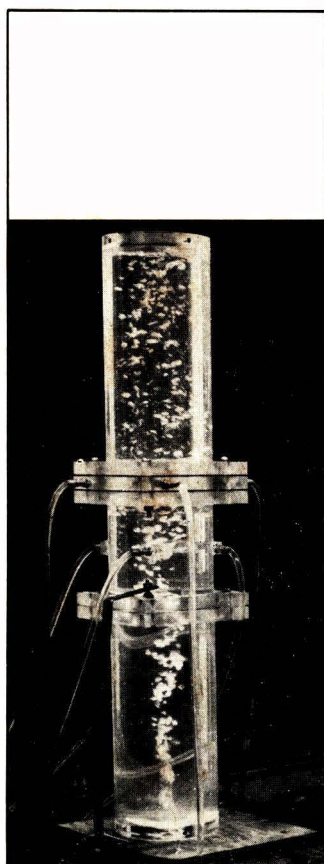
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JULY 1968



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July 1968

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EDITORIAL

Mediocrity need not be the universal common denominator

The antidegradation clause promulgated by Interior says that states should preserve some water systems in an extra fine condition

A storm has been raised by the recent ruling of the U.S. Department of Interior that "Waters whose existing quality is better than established standards . . . will be maintained at their existing high quality." Usually referred to as the antidegradation clause, this provision has been attacked by some who claim it is unrealistic, supported by others who call it imaginative. It has been damned by those who see in it excessive federal interference in states rights, praised by those who feel that the states have had enough time—but have failed—to act on their own.

It has been deplored by those who see it as a threat to free enterprise and the economic opportunity of underdeveloped areas, boosted by those who see it as a rein on the reckless, destructive tendencies of some people to usurp public property for private gain.

There are those who declare that it is improper for the Federal Government first to accept some state water quality standards and then, apparently, to reject them under pressure; but there are also those who feel that it is the responsibility of the Federal Government to adopt a conservative yet flexible approach to the nation's water pollution problems—if, indeed, not to all her problems.

The fact is that law usually starts as a simple thing. Then, as it is tested and found wanting in some way or ways, it is strengthened or corrected. Few of us are sufficiently gifted, either separately or in groups, to prepare for all eventualities. Thus, it is hardly to be expected that imperfect men in imperfect union will achieve perfection in their early attempts to develop water quality standards.

After several states' water quality standards were accepted, and only then, did the question arise: "Are the standards now to serve not only as the minimum acceptable levels to which polluted waters must be raised, but also as levels to which higher quality water may be reduced?"

The question has been answered by Interior, which says that no degradation will be permitted unless Interior is satisfied that such a change is "justifiable as a result of necessary economic or social development . . ." What Interior has said, in effect, is that the worst must be improved, the mediocre can remain that way, and the best is to be preserved.

What are the definitions of "justifiable," "economic," and "social?" Does it really matter? Hardly! The courts are always available to provide relief from unreasonable restraint and unfairly applied laws. And Congress, if it is so moved, can alter the laws itself.

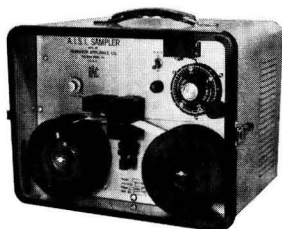
When men make laws they are seeking, usually, a better, more nearly perfect world in which to live. If men have erred—or in this case, if Interior has erred—in the promulgation of water quality goals, it will be better for them to have erred on the conservative-conservation side. Resurrection of a dead or dying lake, stream, or river is a monumental, if not impossible, task. Can anyone put an economic, social, justifiable price tag on Lake Erie? Or on Lake Michigan, which is on the way to join her in depravity?

Anyone who has waded into a clean stream, sailed on a clear lake before a fresh wind, or slaked his thirst at a sparkling spring, surely must often want to make the would-be despoilers drink their words.

William J. Josephs

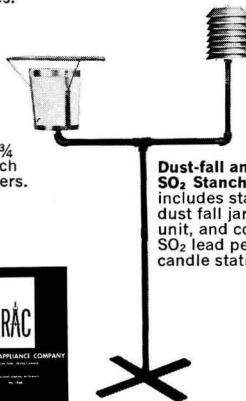
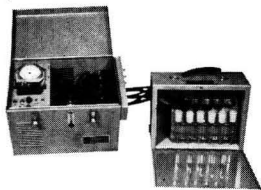
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In these words, Surgeon General William H. Stewart keynoted the first National Conference on Noise as a Public Health Hazard. Warning that in protecting health, absolute proof comes late, Stewart still believes that “we begin our confrontation with noise as a generalized public health hazard on a strong base of knowledge concerning occupational hazards. Specifically, we know that excessive noise exposure causes hearing loss.” Also, he told the Washington meeting, which was supported by the Public Health Service and sponsored by the American Speech and Hearing Association, we know that noise can cause physiological changes. “Still to be explored, of course, is a broad range of problems underlying and surrounding these observations. We need to know more about the mechanisms whereby noise damages hearing. We need to know more about the effects of noise on performance and work efficiency in the job setting. And, of course, we need to extend our knowledge outward into the community where people live—to the world of jackhammers and power mowers and booming hi-ft sets and screeching airplanes that we call home.”

Off Flavor in Dried Milk Is Linked with Air Pollution

Ozone concentrations from 30 to 50 p.p.b. in the air used for drying milk is responsible for serious flavor defects in the dried milk product, according to Dr. F. E. Kurtz, Agricultural Research Service of the U. S. Department of Agriculture. At the recent meeting (Columbus, Ohio) of the American Dairy Science Association, he noted that the combined action of sunlight and heat on automobile exhaust fumes can result in the conversion of considerable quantities of these combustion products to ozone. ARS plans additional experiments this summer to study the off flavor problem.

Water Resources Research Program Total \$2 Million

Thirty two-research projects have been selected for the water resources research program for fiscal 1969, according to Dr. Roland R. Renne, Director of the Office of Water Resources Research. Gleaned from 352 research proposals, these 32 projects concentrate on research related to water resources planning and management and to socio-economic aspects of water resources problems. Seven projects focus on urban water problems; three focus on estuarine problems, four on ground water, two on flood control, and one on urban hydrology. In accordance with requirements of the Water Resources Research Act (P. L. 88-379), the 32 projects have been transmitted to the Congress. After completion of a 60-day waiting period and enactment of the appropriation, final contract and grant agreements will be executed.

Reorganization of HEW Draws Daddario's Criticism

The quality of the environment is not a human health issue, per se, according to the recent report entitled "Managing the Environment" which was prepared by the Senate Subcommittee on Science, Research, and Development. The quality is more a matter of the unacceptability, at face value, of offensive odors, discolored water, low visibility, eye irritation, littered landscapes, and nuisance soiling, the report concludes. Basing its findings on hearings held earlier this year, the subcommittee notes that the progress toward clean air is slowed because of the Public Health Service's preoccupation with human health effects. "We need not wait for precise health hazard definition in order to reduce air pollution," says Rep. Emilio Q. Daddario (D.-Conn).

Within the week following announcement of the recent reorganization of the Department of Health, Education, and Welfare, Daddario said, "The grouping of the National Center for Air Pollution Control with consumer protection services is a step in precisely the wrong direction." Air pollution abatement administration belongs in an engineering atmosphere, according to Daddario. "The engineering operations of air pollution abatement should be transferred to the Department of Interior so that engineering and economic criteria could be considered together with proven problems of human health effects which could continue to be supplied by the Public Health Service," he noted. Already, the congressman has asked the chairmen of appropriate Congressional committees to begin the investigations which will be necessary to relocate air pollution abatement administration in its proper place. Thus, the Department of Interior could be the lead organization for air pollution abatement and for developing a national environmental policy.

HEW Moves for Effective Control of Vehicle Emissions

Proposed standards for 1970 model year motor vehicles (ES&T, January 1968, page 8)—including both domestic and imported automobiles, trucks, buses, and diesel powered motor vehicles—were adopted officially on June 4, with but one exception. Control of hydrocarbon evaporative losses from automobiles and light trucks is deferred until 1971 model vehicles. The 1970 standards control both emissions of hydrocarbons and carbon monoxide, but do not specify limits for nitrogen oxides. Prior to the adoption of 1970 standards, earlier standards required more stringent control of emissions from small cars. But 1970 standards make no distinction between car sizes. Rather, they limit all cars to the same amount of pollutants to be discharged. But, beginning with the 1970 model year vehicles, a number of changes will be made in the test procedure. These changes include:

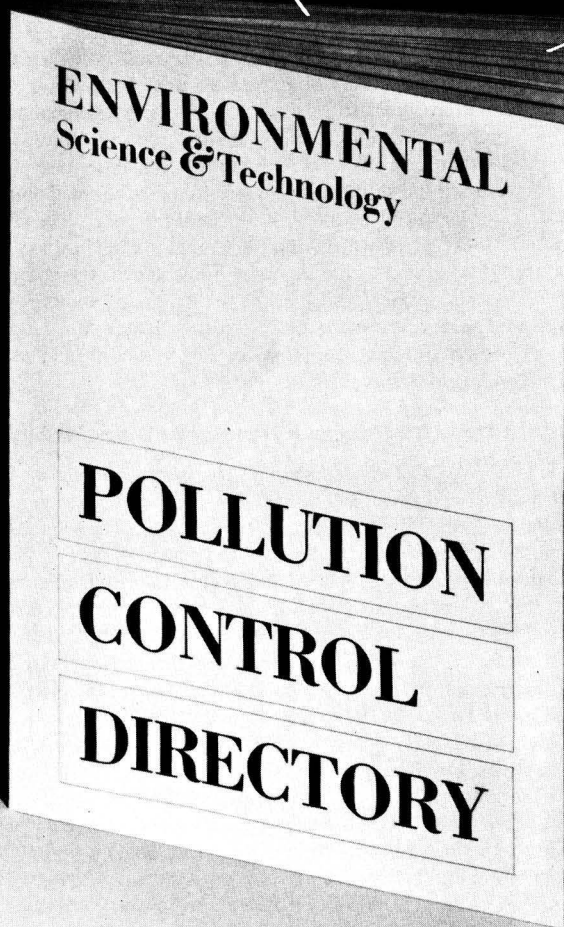
- Separate formulas will be used to calculate the amount of exhaust emissions by vehicles with manual or automatic transmissions. At present, a single formula is used for both. The new formula takes into account the fact that the volume of exhaust gases is greater for vehicles with automatic transmissions and lower for vehicles with manual transmissions than the combined average.
- The procedure used to calculate the average exhaust emissions from a group of test vehicles will be changed. At present, when average emissions from all vehicles in a particular engine size group are calculated, data from each vehicle are given equal weight. Under the revised procedure, data will be weighted in proportion to the anticipated model sales.

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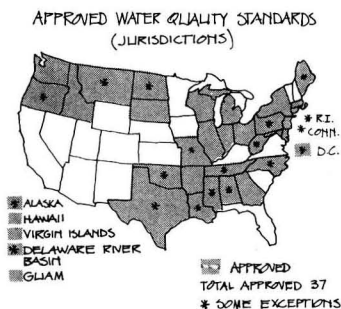
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Reverse Osmosis May Be the Answer to Whey Disposal

Whey, a byproduct of the manufacture of cheese, has no great commercial value and creates a large BOD load when dumped into water systems (ES&T, April 1968, page 265). However, whey may be disposed of by the process of reverse osmosis, according to Frank E. McDonough, Agricultural Research Service of the U. S. Department of Agriculture. Fourteen billion pounds of whey (two thirds of the annual production) are discarded annually. Many states have outlawed dumping of whey in waterways, and others are planning to do so. The reverse osmosis process is especially suited to small volume cheese plants, those producing about 15,000 pounds per year. The process removes from 75–80% of the water from whey, but the clogging of membranes with precipitated solids remains a problem. However, the process could be economically feasible in one to three years, according to McDonough, who bases his estimates on preliminary data from a pilot study. At present, whey is recovered in some cheese plants by a costly concentration procedure using vacuum evaporators.



Major Integrated IBP Program Receives Financial Support

Research on the grasslands biome moves into the operational phase. Under a \$350,000 grant from the National Science Foundation, the grasslands research is the first of a group of high-priority studies of biomes in the U. S. International Biological Program, analysis of ecosystems (ES&T, June 1968, page 415). In announcing the grant, Dr. Leland J. Haworth, Director of NSF, noted that the grasslands study is an innovative approach to ecological research in which scientists will not only be able to analyze the systems as they operate naturally, but will also be able to treat them as laboratories, by measuring changes brought about by man's use of the territory. The study, coordinated by Dr. George M. Van Dyne (Colorado State University), involves a multi-disciplinary team of scientists including meteorologists, hydrologists, systems analysts, agricultural scientists, as well as plant, animal, and microbial ecologists. Using modern techniques of remote sensing and systems analysis, these scientists will carry out carefully coordinated field and laboratory experimentation at the grasslands site, which includes the 15,000 acre Central Plains Experimental Range operated by the Agricultural Research Service and a 110,000 acre portion of the Pawnee National Grassland operated by the U. S. Forest Service.

The ecological system of the grasslands will be analyzed in terms of four components:

- Abiotic or nonbiological factors such as climate, soils, and water.
- Producers (vegetation; the organisms that produce food). Photosynthesis will be carefully measured under field conditions, as an essential step to evaluate the basis of productivity of the plant community.
- Consumers (animals; the organisms that consume food). The comparative diets of both large and small plant-eating animals will be closely examined to learn how various animals convert photosynthetically produced materials to products that are useful to man.
- Decomposers (microorganisms; the organisms that degrade dead animal and plant tissue into nutrients available for important life cycles). Initial studies will focus on bacteria and fungi and their relationships to the carbon and nitrogen cycles.

Pollution Control Service Becomes Available

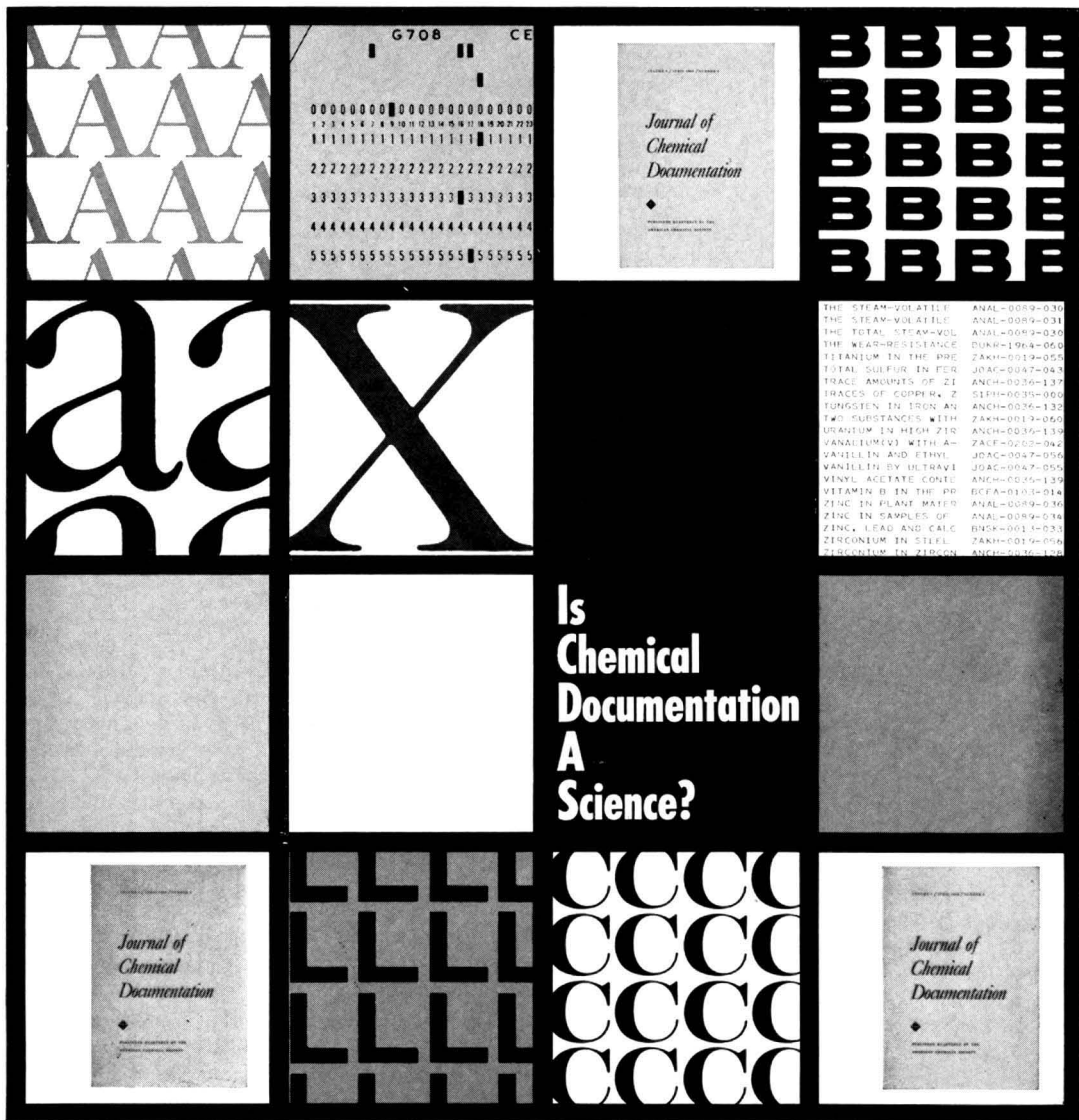
The first estuarine prediction service in the U.S. centers on water pollution in the estuarine area of Maine. Conducted by the Environmental Science Services Administration of the Department of Commerce, the service will provide advance forecasts twice a month and include the following data:

- Advance warning of possible pollutants passing through the estuary.
- Flushing rate which will give the number of days required for fresh water or suspended matter to travel from selected points along the estuary. These forecasts will be made available to both governmental and municipal agencies and private industry who are concerned with water pollution control as it affects fisheries, public health, recreation, potable and industrial water, residential and industrial development, and the like. Initially, service for the one-year pilot program will issue data for the Penobscot River and Bay Estuary, says Charles R. Muirhead, acting chief of the predicting service.

Steam Cars Will Reduce Air Pollution and Noise

The steam car of today is competitive with the internal combustion powered car. But failures in the market system, such as the existence of monopolies or quasi-monopolies, tend to eliminate or reduce competition. And it is for this reason that external combustion engines are not as far along today as they might be—all this according to Dr. Robert U. Ayres, Resources for the Future, Inc., testifying at recent joint hearings on technological capabilities and future potentialities for external combustion engines before the Senate Committee on Commerce and Senate Subcommittee on Air and Water Pollution. Using steam or some other vapor, external combustion engines would virtually eliminate automotive air pollution and greatly reduce engine noise. Furthermore, they are safe and would be cheaper to manufacture, cheaper to drive, and easier to maintain than internal combustion engines because they eliminate the transmission, clutch, starter, carburetor, distributor, and many other complicated auxiliary systems.

The Williams Engine Co. (Ambler, Pa.) has invested more than 30 years and \$2 million in the design, research, and development of steam power systems for motor vehicle use. One of their prototype steam cars, with 25,000 miles on it, was tested (December 1966) in the 7-mode California cycle test. The emissions data were: • Hydrocarbons, 20 p.p.m. • Carbon monoxide, 0.5%. • Nitrogen oxides, 40 p.p.m. At the hearings, the Williams brothers, Calvin and Charles, said that their company is presently inactive because of a lack of operating capital. Their attempt to move from R&D into sales and production proved more costly than they had anticipated. Richard S. Morse, chairman of the Department of Commerce committee which prepared the report "The Automobile and Air Pollution: A Program for Progress," said that with the improved base of knowledge now available in this field, there is no reason why the development of steam technology could not be expedited by the normal route of R&D contracting or the purchasing of demonstration units. For example, the Federal Government purchases approximately 80,000 motor vehicles annually, at a cost of \$175 million. Perhaps, he notes, the Federal Government could purchase steam cars. But Herbert L. Misch, a vice president of the Ford Motor Co., said that the steam engine is more complex than the internal combustion engine. The complexity index rating for the steam engine is 46; for internal combustion engines, 35, according to Misch.



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Mining Industry Fights Federal Controls

Because reclamation conditions vary widely, requirements must be tailored for each area; besides, surface mining does not create interstate effects, says mining industry

The Surface Mining Reclamation Act of 1968—another of the administration backed, urgently needed, legislative proposals for the protection of our environment (ES&T, March 1968, page 168)—authorizes a joint federal-state program for the regulation of all surface mining. S. 3132 found support in witnesses from governmental departments, but met sharp opposition from industry witnesses at recent hearings of the Senate Committee on Interior and Insular Affairs.

The Senate bill does not include provisions for the reclamation of previously mined lands. Within two years of the date of enactment of S. 3132, individual states would be given the first opportunity to tailor suitable surface mining control programs to their local needs. S. 3132 specifies:

- Federal Government funding up to 50% of a state's cost for developing, administering, and enforcing a state's plan.
- Federal regulations would be imposed if a state failed to act. Current and future mining operations come under S. 3132 if the products are used in interstate commerce.

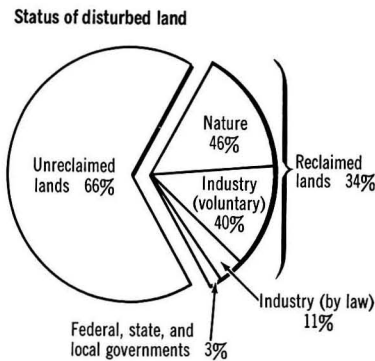
In a manner similar to Interior's procedure for review and approval of water quality standards, reclamation standards would be developed by each state in accordance with appropriate needs and then received and approved by the Secretary of Interior. One key provision that each state must meet is the requirement for adequate bonding and enforcement.

In recent testimony, Secretary Udall said that his department's main concern is to insure that tomorrow's inventory of damaged lands is not larger than today's. In the past, 3.2 million acres of land have been affected by surface mining and less than one third of this acreage has been even partly reclaimed, according to Interior.

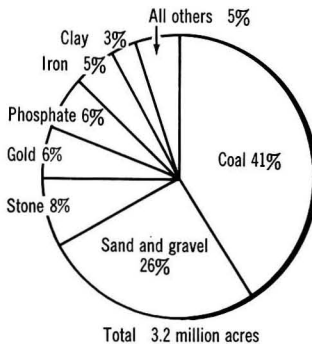
"At present, some 20,000 surface mines are in operation, and their op-

erations affect 150,000 acres of land each year. By 1980, some 5 million acres will be affected by operations involved in producing minerals needed in our economy, according to Udall. For this reason, Udall feels that associated bills, S. 217 and S. 3126, each of which deals with the reclamation of already damaged lands, should come later.

More than 3 million acres have been disturbed by surface mining since January 1965



Mining activity leading to disturbed land



Source: Department of Interior

"Clearly, it is imperative that we provide measures to prevent needless damage to our land and other natural resources," Udall says. Each state has had some surface mining activity within its boundaries. Only 14 states have laws relating specifically to the conduct of surface mining operations and the reclamation of surface mined areas, and five of these direct their attention only to coal mining.

In 1965, 35% of our coal, 80% of our copper, and 90% of our iron ore came from surface operations. Overall, 80% of our mineral production tonnage comes from surface mines.

Categorically, mining witnesses opposed federal control of surface mining. Joseph S. Abdnor, spokesman of the American Mining Congress, told the committee, "Despite disclaimers to the contrary, S. 3132 would effectively take over the field of oversight of surface mining for the Federal Government and would impose unwarranted costs on both industry and the federal treasury." Also, Abdnor continued, "The damage to privately-owned and state lands by surface mining does not produce interstate effects as does the flow of water and the shifting of air. The enforcement of federal controls over such land use would be a remarkable extension of federal power."

Coal mining witnesses told the committee that their industry does not want to be saddled with new federal regulations which would impede the remarkable progress now being made in land reclamation. Edwin R. Phelps, Peabody Coal Co. (St. Louis, Mo.), said that his company operates in eight states, of which six already have strip mining reclamation laws and the other two have them under study. "These requirements are not all uniform, and they must be different, due to the extreme variation in the condition of the areas to be reclaimed and the results expected," Phelps commented.

Lake Erie Pollution Control Program on Schedule

June enforcement conference highlights progress on treatment plants, but issues of phosphate control, offshore drilling, and dredging disposal yet to be faced

The Lake Erie Pollution abatement program is "moving apace," and "we are beginning to see the light at the end of the tunnel," summarized the chairman of the Lake Erie Pollution Enforcement Conference which met in Cleveland last month. After hearing progress reports on the construction of water treatment facilities in the five-state lake basin by federal, municipal, and industrial installations, U. S. Dept. of Interior's Murray Stein concluded that the programs are substantially on schedule, and in the few minor cases of noncompliance, corrective measures are being taken.

Whatever the optimism about the progress on treatment plants on the lake's tributaries, the meeting did highlight a few of the thorny issues yet to be faced in the Lake Erie program. Only one of these, the matter of updating a previous conference recommendation on phosphate removal, was formally considered by last month's conference. No action was taken, pending a future technical session.

But the committee did hear a progress report on the problem of disposal of dredging spoil from Lake Erie harbors, a perennial and perhaps the most controversial aspect of the Lake Erie pollution problems. In addition, the conferees listened to some sharp criticism of the granting of leases for offshore oil and gas drilling.

The current operative recommendation on phosphate control of the Lake Erie conference, established at a 1965 session, calls for treatment plants to "maximize the removal of phosphates." At the recent meeting, Stein polled the conferees as to the possibility of setting specific requirements for phosphate removal, with a view toward presenting a unanimous conference recommendation to the Secretary of Interior. He pointed out that the 1965 recommendation had become inadequate in the light of recent findings regarding the feasibility and economics of better-than-80% removal of phosphates (ES&T, March 1968).

Conferees from Michigan and Indiana, who had already approved an 80% stipulation on phosphate removal in the Lake Michigan enforcement program, were willing to approve a similar recommendation for Lake Erie—as were the delegates from Pennsylvania. Delegates from New York and Ohio, however, while not opposed to the 80% limit in principle, felt they were not yet ready to commit their states to a timetable for 80% compliance. They called for an additional technical session on the matter.

Earlier in the session, Rep. Richard D. McCarthy of New York addressed the conferees to call for action by the Federal Water Pollution Control Administration on the matter of offshore drilling for oil and gas in Lake Erie.

Rep. McCarthy termed it "most unfortunate" that Pennsylvania is moving ahead with the awarding of drilling contracts. He pointed out that New York and Ohio, which also have economic interest in Lake Erie's offshore resources, have postponed plans to lease bottomlands pending further investigation, and that Michigan has stated it will not lease lands in Lake Erie for mineral development.

McCarthy called for FWPCA to intervene, on the basis of existing authority, in the proposed oil and gas exploration. He added that the whole question of oil pollution control is now being considered by Congress, and enactment of legislation will have a bearing on drilling in Lake Erie.

The U. S. Army Corps of Engineers' program to investigate alternatives to the open-lake dumping of spoil dredged from Great Lakes harbors was outlined at the meeting by Col. Amos L. Wright, district engineer of the Corps' Buffalo district. This program was initiated in 1966 at the request of the Bureau of the Budget. The bureau asked for the study after the Corps presented a \$95.6 million program to the bureau for the construction of diked disposal areas at the 15 most polluted harbors of the Great Lakes.

The Corps has received \$6 million to date for the study, and expects to receive additional funds to allow them to complete the study in the next fiscal year. The pilot program is underway at eight localities on the Great Lakes, four of them on Lake Erie. Alternates to open-lake dumping being studied include the creation of diked disposal areas from slag and crushed rock, disposal in pits, mines, and other areas away from the lake, as well as the testing of various methods of treating the effluent from the disposal operation.

FWPCA is participating in the Corps' program by sampling, testing and analyzing the materials to be dredged and the surrounding waters.

As to the Corps' 1968 dredging under the pilot program, Col. Wright stated that at polluted harbors, open-lake dumping will not be used wherever alternate disposal areas are available. At the three Lake Erie ports where FWPCA has determined that there are no pollutants in the material to be dredged, the spoil will be disposed of in authorized disposal areas in the lake, as will materials from other harbors where alternative disposal areas could not be found and where postponement of maintenance dredging would be an economic hardship to a port or a region.

A Lake Erie water quality management model was called for by one of the conferees, Walter A. Lyon, director of the Pennsylvania Department of Health's division of sanitary engineering. According to Lyon, "one of the least understood areas of the therapeutics of Lake Erie is the cause and effect relationship between the hydrology, the inputs and outputs of degrading substances, and the aquatic life and biochemistry of the lake." He feels that these must be mathematically related in a conceptual framework for public policy making. He also feels that it should be possible to develop a computer program to predict the consequence of changing the parameters of the Lake Erie ecosystem.

Fluid Bed Incinerators Studied for Solid Waste Disposal

The versatility of fluid bed waste incinerators means that cities can use them to dispose of sewage sludge, refuse, solid industrial wastes, and liquid and gaseous wastes

Fluid bed incinerators are getting serious consideration as a solid waste combustion technique. Fluid bed units have already established themselves in the field of sewage sludge incineration, and a few units have been installed to burn industrial wastes. Now, the method is being talked about as a means of attacking the broader and more complex problem of solid refuse disposal.

At a recent meeting of the American Society of Mechanical Engineers' incinerator division in New York City, Prof. Alfred F. Galli presented the results of studies conducted at West Virginia University. These studies were designed to show that fluid bed incineration can be a compact method for the clean combustion of solid waste materials. The West Virginia work is being conducted under a demonstration grant from the Department of Health, Education, and Welfare's solid waste program. Galli and his coworker, Prof. Richard C. Bailie, concluded that all experimental results to date have been positive and support possible advantages of fluid bed incinerators.

In addition, Pope, Evans & Robbins, a consulting engineering company that has been studying fluid bed combustion of coal, is hoping to extend their work to the combustion of solid waste. Shelton Ehrlich, project engineer at Pope, Evans & Robbins' applied research division in Alexandria, Va., says, "We are just getting a feel for the solid waste incineration aspect, but we definitely see a potential for fluid bed incineration of untreated and unsorted solid municipal waste."

Natural extension

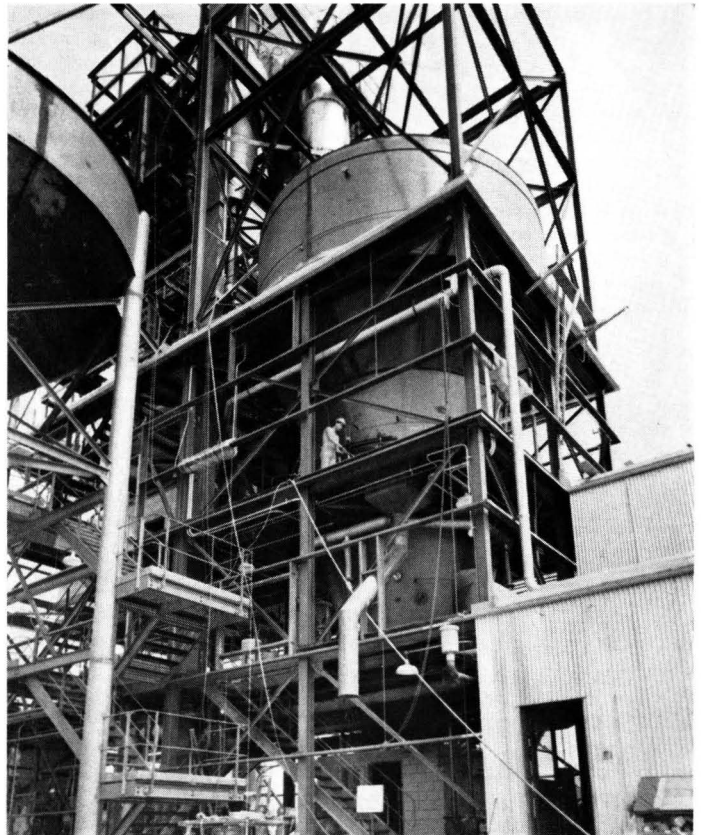
Fluid bed combustion is a natural extension of experience with fluid processing techniques commonly used in the chemical processing industry. Be-

cause of the intimate contact that can be obtained between a solid and a fluid phase in these units, fluid bed techniques have become the basis for many industrial chemical reactions and have been applied to a wide variety of separation problems.

The past few years have seen much work on the application of fluid bed principles to combustion techniques.

Both in the U.S. and abroad, industrial and government institutions have been working on the combustion of coal for steam boilers. The U.S. Bureau of Mines, for instance, has such a program in Morgantown, W. Va.

Some work on applying fluid bed combustion to waste incineration has already achieved success. Dorr-Oliver Co. of Stamford, Conn., has developed



Pulp liquor. Dorr-Oliver FluoSolids reactor incinerates spent sulfite pulping liquor. Such units allow recovery of inorganic pulping chemicals in pelletized form

and is marketing its FluoSolids reactor for the combustion of sewage sludge. Since the installation of the first such unit at Lynnwood, Wash., in 1963, the company has installed more than 30 in the U.S. and overseas. Most of these units were built for incinerating sewage sludge, but a few have been used to handle industrial wastes such as spent coffee grounds and pulp-ling liquors.

Fluid bed problems

But much work has yet to be done before fluid bed techniques can be applied to the combustion of a material as complex and nonhomogeneous as solid municipal waste. For one thing, more efficient feeding methods have to be developed, as well as ways to remove the ash and unoxidized materials from the bed. Other problems relate to maintaining an air distribution that keeps solids of varying size and density in suspension in the bed.

As difficult as these problems are—and they are formidable—the potential advantages of applying fluid bed combustion to municipal waste could well justify an attempt at their solution.

Fluid beds are, in general, compact solids-handling devices, relatively simple to operate and control. And fluid bed incinerators are probably cheaper to construct than conventional grate-fed incinerators.

Combustion within a fluid bed is rapid and complete, with a minimum amount of undesirable combustion products. The high degree of combustion that can be obtained with minimum quantities of excess air reduces the size of gas handling and cleanup equipment. In addition, the high heat transfer rates that can be obtained improve the feasibility of generating steam from solid waste combustion.

Three-part system

A typical fluid bed reactor consists of the following:

- A lower chamber for distributing the fluidizing gas.
- A middle section where the bed material is kept in suspension by the fluidizing gas and where the desired reaction occurs.
- An upper section where the gas passes out of the bed.

In a fluid bed furnace, the bed material consists of high-fusion temperature particles, such as silica sand. The

fluidizing gas is air, which also supplies oxygen needed for combustion.

The bed particles absorb the heat of combustion and also act as a large heat sink, which can rapidly transfer heat to the solid feed. Thus, when a solid combustible material is placed in the reactor, it quickly absorbs heat until it reaches its ignition point—so combustion is rapid and virtually complete.

The violent agitation of the particles within the bed of the furnace gives rise to several desirable characteristics. The high heat capacity of the bed particles and their rapid movement throughout the reactor maintain a fairly constant bed temperature.

With the high heat transfer rates which can be obtained, combustion can occur before any appreciable distillation products are lost. Those that do evolve are consumed within the bed, and little or no unburned hydrocarbons are present in the stack gases.

High combustion efficiencies occur at relatively low and uniform temperatures, with the result that very little oxides of nitrogen are produced.

Since refuse generally has a low sulfur content, the only objectionable combustion byproducts would be particulate matter. With relatively little excess air required for combustion, the volume of stack gases that must be treated is greatly reduced.

Reduced air needs

The need for low quantities of excess air is perhaps the major advantage of fluid bed incinerators. Hot spots in the combustion zones of conventional incinerators can develop temperatures as high as 1800° F., and such high tem-

peratures cause slagging on the walls of the incinerator and interfere with its operation.

In the operation of conventional incinerators with refractory walls up to 250% excess air is often used to limit the maximum temperature within the combustion zone. Equipment to handle these volumes of combustion gases and scrub them clean of fly ash to meet increasingly stringent air pollution control regulations can run to about one third the capital cost of a conventional incinerator.

Some modern units incorporate cooling water jackets in the walls to control the wall temperature and thus reduce the excess air requirements to between 50 and 60%. By contrast, fluid bed incinerators may be able to operate with as little as 5% excess air.

With low quantities of excess air used to support combustion, the heat of combustion must be removed from a fluid bed furnace by other means. One possibility that has been suggested is the recovery of waste heat for steam and power generation. West Virginia's Bailie believes that with the heat transfer rates that occur within the bed, perhaps up to 50% of the heat of combustion can be recovered through the walls.

Other fuel requirements

Because of the widely varying composition of refuse, it is doubtful that a fluid bed refuse incinerator designed for waste heat recovery could operate without an auxiliary fuel to maintain stable bed temperatures. However, fluid bed furnaces could accept a variety of auxiliary fuels. Waste low grade coal, not acceptable for conventional boilers,



Sewage sludge. First commercial fluid bed unit for burning sewage sludge was installed at Lynnwood, Wash. Ash product from incinerator is used for landfill

could be mixed with the solid feed to increase the heating value, or liquid or gaseous fuel could be sprayed into the bed to maintain constant temperature control.

Such versatility stems from the fact that the rate of power generation in a fluid bed unit is controlled by the bed temperature and the air flow rate that causes the motion of the inert bed particles. The fuel used has a relatively minor effect as long as it can burn at a rate sufficient to maintain the bed temperature.

West Virginia demonstration grant

Under the HEW demonstration grant project, which is slated for completion this year, the West Virginia group hopes to demonstrate the feasibility of continuous combustion of a large variety of materials in fluid beds. Preliminary data runs have been made with solid fuels such as coal, and have demonstrated that volumetric generation rates of 100,000 to 150,000 B.t.u./hour/ft.³ can be realized.

In the pilot unit, the volumetric generation rate is limited by the ability to remove heat (no provision is made in the present unit). Other factors which could improve the volumetric

generation rate include larger or more dense bed particles. However, the quality of fluidization is reduced for heavier particles, and combustion and heat removal would be less efficient.

Optimum size for bed particles used in burning solid refuse has not been determined, and is part of the continuing program.

Feeding solid refuse

The major problems encountered with fluid bed incineration for solid refuse are those associated with feeding material into the unit. The only feeding techniques evaluated in the West Virginia project—continuous flight and segmented flight screw conveyors—were unable to feed mixed refuse on a continuous basis for extended periods. Thus, it has not yet been possible to evaluate the combustion of mixed refuse intensively.

The West Virginia workers admit that some pretreatment, such as sorting and shredding of the solid waste feed may be necessary. But Baillie points out that the problems involved with feeding the small pilot unit would not be as great with a larger unit of the size being contemplated for a commercial scale incinerator.

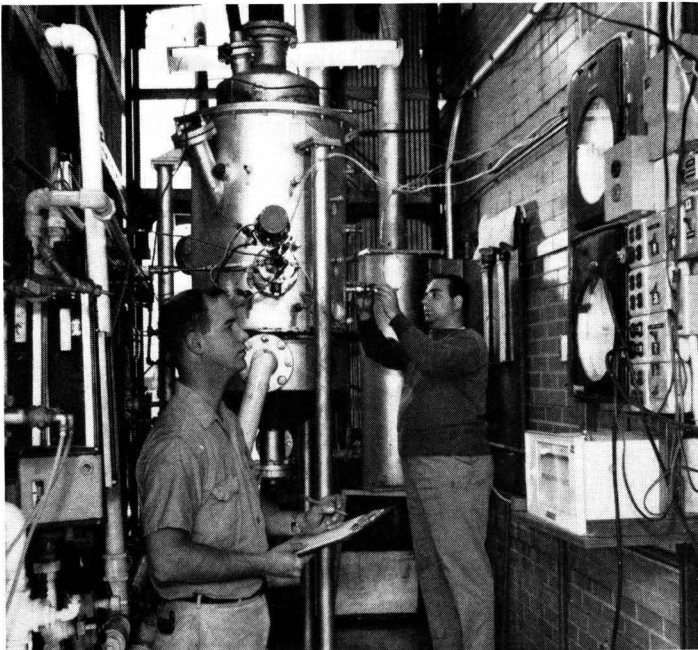
Larger screw feeders would undoubtedly be more efficient. And the use of piston feeders is also being considered. Piston feeding would not, of course, be uniform. But stroke cycles of less than one minute would not create prohibitive fluctuations in the bed temperature. Further uniformity could be obtained by multiple piston feeding.

The workers at Pope, Evans & Robbins also conclude that feeding and ash removal are major problems associated with fluid bed solid waste incinerators—although quickly admitting they are not the only ones.

Air distribution problems arise from the necessity of keeping nonuniform particles in suspension in the bed with a uniform air velocity. One solution Ehrlich suggests is a packed fluidized bed, with larger particles falling through and traveling under the fluidized bed on an oscillating grate. Removal of unoxidized material and ash from the bottom of the bed would be accomplished by means of a pulsating air damper that would periodically defluidize the bed in frequencies of about 3 cycles per minute.

Baillie points out that the future potential of fluid bed waste incinerators lies in their versatility. In addition to being the only modern technique for the firing of refuse, the fluid bed incinerator would provide municipalities with a means of handling a variety of disposal problems. For fluid bed incinerators are unique in that they can handle almost any solid wastes, such as sewage sludge, refuse, and solid industrial wastes, as well as liquid and gaseous wastes. (The West Virginia feasibility studies are based on the possibility of a 12 to 14 feet diameter unit, capable of firing about 10 to 12 tons of refuse per hour.)

Pope, Evans & Robbins is equally optimistic. The company envisions a fluid bed incinerator, capable of burning up to 1000 tons of refuse per day, that could be factory assembled and loaded on a rail car for shipment. Combustion intensity would be more than five times as great as in a conventional unit of equivalent capacity. The fluid bed unit would be cheaper to construct, and, in spite of the relatively high cost for fan power for the fluidizing air, operating cost would probably be no greater than in a conventional incinerator.



Solid waste. Pilot scale incinerator at West Virginia University is being used to study fluid bed combustion of a variety of solid waste materials

Waste Problems of Agriculture and Forestry

Finding solutions consistent with rapidly changing concepts of environmental quality related to health, social, and economic goals will not be easy

A few decades ago, animal manure was considered a tremendous asset in making farm soils fertile. Today, a farmer usually finds it cheaper to build up soil nutrient levels by applying synthetic fertilizer from a bag. So, manure accumulates in animal pens in vast quantities. Thus, says a recent Department of Agriculture report, the market place has changed what was once a resource into a waste disposal problem.

The report, "Wastes in Relation to Agriculture and Forestry," surveys 10 major contaminants of air, water, and land soil produced by agriculture and forestry, and how the contaminants affect the two industries in turn. In addition to animal wastes, other organic wastes—such as forest, crop, and processing residues—are also produced as byproducts of the two industries. These substances, carried in water, incur a high biochemical oxygen demand. Dry on land, they can burn, produce odors, or attract flies and vermin.

Big business creates big problems

Domestic animals in the U.S. produce close to 2 billion tons of wastes annually, including excrement, used bedding, paunch manure from abattoirs, and dead carcasses. This quantity of wastes is equivalent to that produced by a human population of 1.9 billion. As much as 50% of this waste is produced by large-scale, confinement-type enterprises. A feedlot handling, for example, 10,000 cattle, accumulates 260 tons of solid and 100 tons of liquid wastes daily. Such large concentrations of animals have greatly magnified the problems of handling wastes, including health hazards and esthetic nuisances.

Removing the waste from animal quarters, transporting it, and—where feasible—spreading it on land represent a significant cost to the meat producer. For example, the manager of a million-bird egg laying operation in Mississippi estimates his annual waste handling costs at \$100,000 or 10 cents a bird. A 1961 Michigan study indicates that beef feedlot operators spend \$3.43 per head marketed and dairymen \$9.29 per head for waste removal and spreading.

Despite these expenditures, operators are encountering problems. As suburbanites move into agricultural areas, they protest against accumulations that give off malodors. The report cites the example of a 27,000-head beef cattle feedlot in Milford,

Tex. The owners had purchased enough land, well out in the country to provide what they thought to be an adequate buffer zone between the lot and the other rural residents. Eleven damage suits averaging about \$15,000 each have been filed against them. Four have been settled, the court allowing claims ranging from \$2500 to \$7500.

In another instance, the New York State Supreme Court issued a temporary injunction against a large poultry producer in Sullivan County. The injunction restrained the producer, a major employer in the county, from allowing noxious odors to permeate the air of two adjoining resorts pending the outcome of a \$125,000 lawsuit against the producer.

Big business. *Health hazards and esthetic nuisances have been created by the new large-scale, confinement-type enterprises for feeding domestic animals. This 6000-animal feedlot collects 150 tons of solid and 60 tons of liquid wastes daily*



New approaches needed

A major research effort must be undertaken to find economically justifiable and esthetically acceptable answers to these new, large-scale problems. There is, according to Agriculture's report, a pressing need to develop basic design criteria that can be used in different situations in different parts of the country.

Among the general areas that must be studied: characteristics of manures; removal from livestock quarters; storage; transport; feasibility of use on land; and disposal by burning, using lagoons or similar facilities, or burying. The report lists the following specific research goals:

- Identify and destroy odor-producing bacteria prevalent in manures.
- Treat manure to make it less attractive as a breeding ground for flies and vermin.
- Develop better procedures for applying manure to cropland. Odors must be controlled in storage, and distribution and runoff water must not be contaminated.

Forest trash

In an average year, 25 million tons of logging debris are left in the woods. This debris serves as a reservoir for

Clean-up. *Infectious agents from agriculture pose public health problems. This dairy feedlot is scraped clean then disinfected to kill such organisms as those causing tuberculosis and brucellosis*

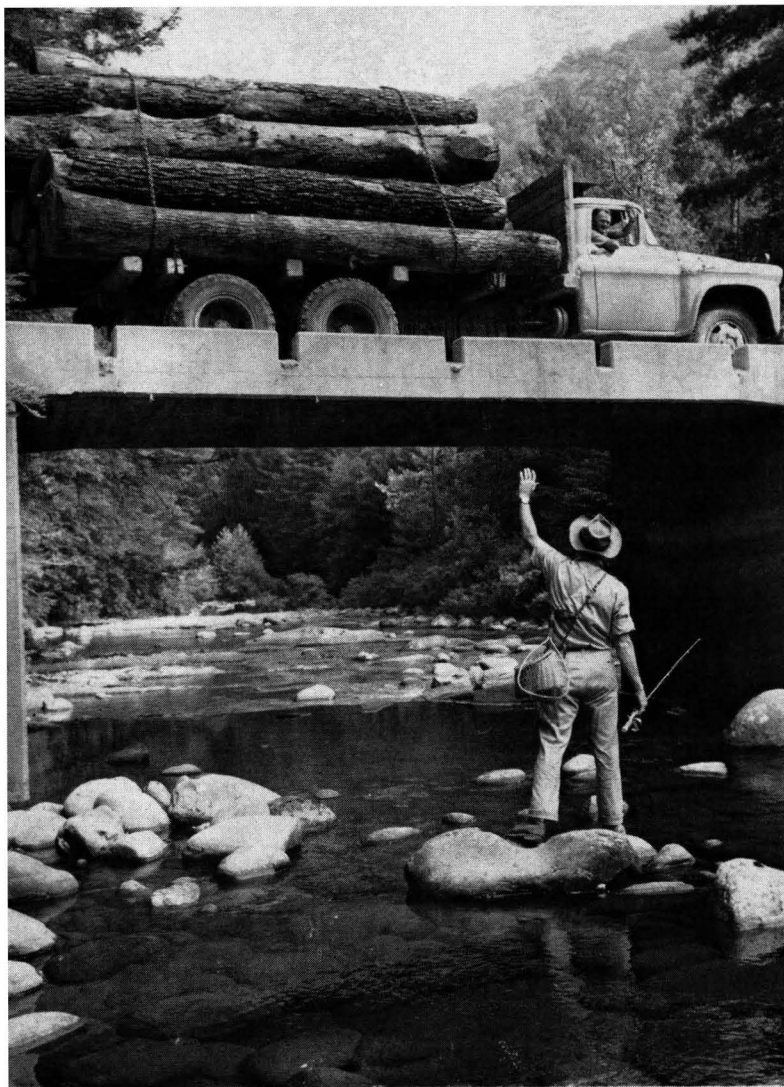


Piles. *Logs find their way to a mill, but left behind are millions of tons of debris. This debris serves as a reservoir for tree diseases, a harbor for insects, and a serious fire hazard. Some of the most disastrous forest fires in North American history started in slash left from logging and land clearing. At present, the material is disposed of by controlled burning, which creates air pollution problems*

tree diseases, a harbor for insects, and is also an exceedingly serious fire hazard. The average size of forest fires originating in logging waste is more than seven times the average size of fires originating in uncut areas where trash has not accumulated.

At present, controlled burning is the only economically feasible technique for disposing of forest trash en masse. However, both controlled and wild fires produce air pollution. (Wild fires yield more smoke and hydrocarbon because the oxygen deficiency is usually greater during wild burns.)

But even prescribed burning causes problems. For example, Oregon-Washington apple growers have filed suit against the U.S. Forest Service. The growers claim smoke from prescribed burning prevents proper apple coloration. Such smoke has also limited recreational areas and activities and has caused reduced visibility on highways and airfields.



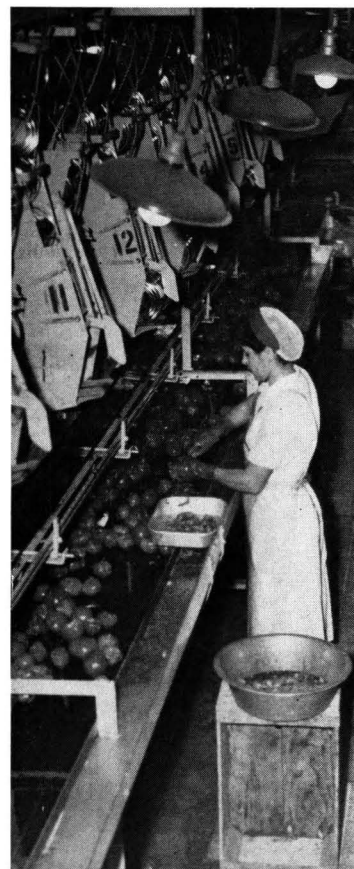
Togetherness. *Commercial operations and recreational activities need not run counter to each other, as this logger and fisherman show*

Processing waste

Processing agricultural and forestry products yields a variety of oxygen-demanding wastes from many sources, among which are: runoff or effluent from sawmilling; process materials from pulp, paper, and fiberboard manufacturing; washing and cleansing water from fruit and vegetable canning. Also included are the contaminated waters that are associated with cleaning dairies, slaughtering and processing of meat animals, tanning, manufacturing cornstarch and soy protein, sugar refining, malting, fermenting, and distilling scouring wool, and wet processing in textile mills. On entering a stream, these wastes make the water unpleasant to taste, smell, or, in many cases, revolting to look at.

The total contribution of processing wastes to water, air, and land contamination is tremendous. The oxidative requirements of the effluent from the woodpulp, paper, and paperboard industries alone exceed the oxidative

Processing. *Oxygen-demanding wastes are produced from processing of agricultural products, such as this tomato canning operation*

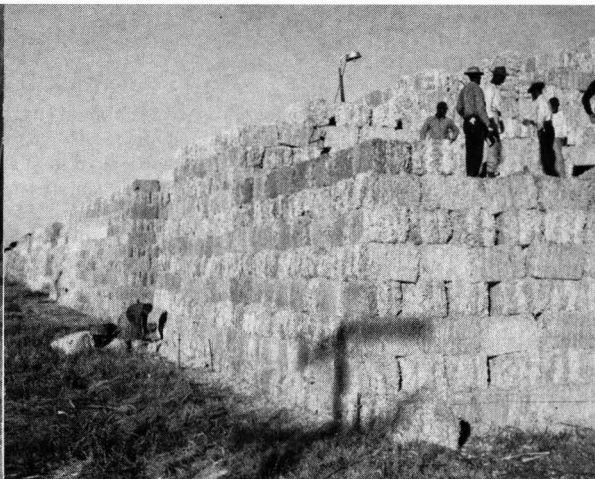


Plant residues

Agricultural wastes from orchards, grainfields, and rangelands, especially in the western U.S., are burned—the most widely accepted way to rid the land of such wastes. It is by means of the smoke and other air pollutants that, at least in one way, plant residues contribute to pollution. A second way is their acting as reservoirs of plant diseases and agricultural pests.

As agricultural land in the U.S. becomes more limited and agricultural activities grow more intensive, the

danger of plant debris carrying diseases and pests to succeeding crops increases. Control of plant diseases, preferably by developing disease resistance or by other nonchemical means, could solve the disease problem. But until then, burning of residues will continue to be common practice. Although, as the report points out, problems pertaining to handling of crop residues are not top priority items, new and better information is needed to handle these wastes more economically and with fewer harmful side effects.



Useful product. *Converting processing wastes into commercial products is the ideal solution to waste abatement. Some sugarcane bagasse is used as fuel in the factory, but most is dried, baled, then sold to be made into insulation board*

requirements of the raw sewage from the entire population of the U.S.

Research has contributed to abatement of processing wastes in three ways:

- Development of useful products, such as making insulating board out of sugarcane bagasse. Because of the potential economic value of such wastes, high priority should be assigned research in this area, according to the report.

- Improvement of processes so that less waste is produced. An example of such an improvement is the new polysulfide modification of the kraft process that yields more pulp while creating less waste, air pollution, and water pollution. The potential for reduction in pollution sources by process modification is exceedingly high. Many steps in processing were developed before much attention was paid to stream contamination by effluents, and probably could be changed to reduce pollution.

- Development of ways of treating wastes before disposal in streams. (Oxidative lagoons, for example, that hold such processing wastes are used effectively to reduce the quantity of organic wastes being dumped into streams.)

Infectious agents

Throughout history, water contaminated with infectious agents has caused human disasters. And such disasters can still happen. In 1965, 18,000 residents of Riverside, Calif., were infected with *Salmonella typhi-*

murium that had entered the city's drinking water. The city's water comes from deep wells, a source presumed to be beyond bacterial contamination. No set of conditions has been found to explain satisfactorily how the water supply became contaminated.

Throughout the nation similar problems are arising. Yet, in view of the large livestock population in the U.S. and the number of livestock diseases that could afflict man, the actual number of infections in the U.S. from drinking water is exceedingly low. During the period 1946-60, only 16

human deaths in the U.S. were attributable to waterborne agents—eight from typhoid fever, four from chemical poisoning, and four from infections other than typhoid.

But as population increases, livestock population will also increase and become even more concentrated geographically. Consequently, greater opportunity will exist for environmental contamination by disease-producing agents from animal sources. In some areas, this source of pollution is already a very serious matter. Recent assays on water from the upper

Marking. *Agriculture has suffered great losses from infectious agents. An economical and effective plan for screening market cattle for brucellosis involves tagging each cow three years old (or older) before it is sent to market*



Potomac Basin indicate that most of the bacterial pollution of this river system comes from nonhuman sources.

Agricultural losses caused by infectious agents carried by air, water, and soil have been heavy. Among the diseases transmitted and which may affect humans are leptospirosis, salmonellosis, brucellosis, tuberculosis, mastitis, and infectious bronchitis. Some progress has been made in controlling such diseases but much remains to be done.

Plant disease agents

Diseases of crops, ornamentals, and trees have caused losses in billions of dollars, despite extensive research to reduce and eliminate the disease agents. Many of the diseases are transmitted by air, water, or soil movements. Control of plant disease agents still has a long way to go. For example, although the potato blight epidemic that caused starvation and misery in Ireland occurred more than 100 years ago, very little is known about the spread of such plant disease epidemics by a contaminated environment. Also, Dutch elm disease and Chestnut blight still leave magnificent trees dead as the diseases sweep the countryside.

Allergens

Close to 12.6 million people annually suffer from asthma or hay fever, notes the Public Health Service. Most cases are due to allergenic pollens. Still, there is little research designed specifically to control plant species that produce allergenic pollen. In fact, there is no complete catalog of allergenic pollen. Much has been learned about control of ragweed, for example, through observations made incidental to other research projects. However, the knowledge has not been put to use in a widespread control operation. Such a program would be necessary for adequate control, since ragweed seed is disseminated by wind and can remain viable in soil for a long time.

Other contaminants

The Dept. of Agriculture report discusses 10 major categories of contaminants to the environment in relation to agriculture and forestry. They are:

- **Radioactive substances.** Agriculture and forestry contribute very little

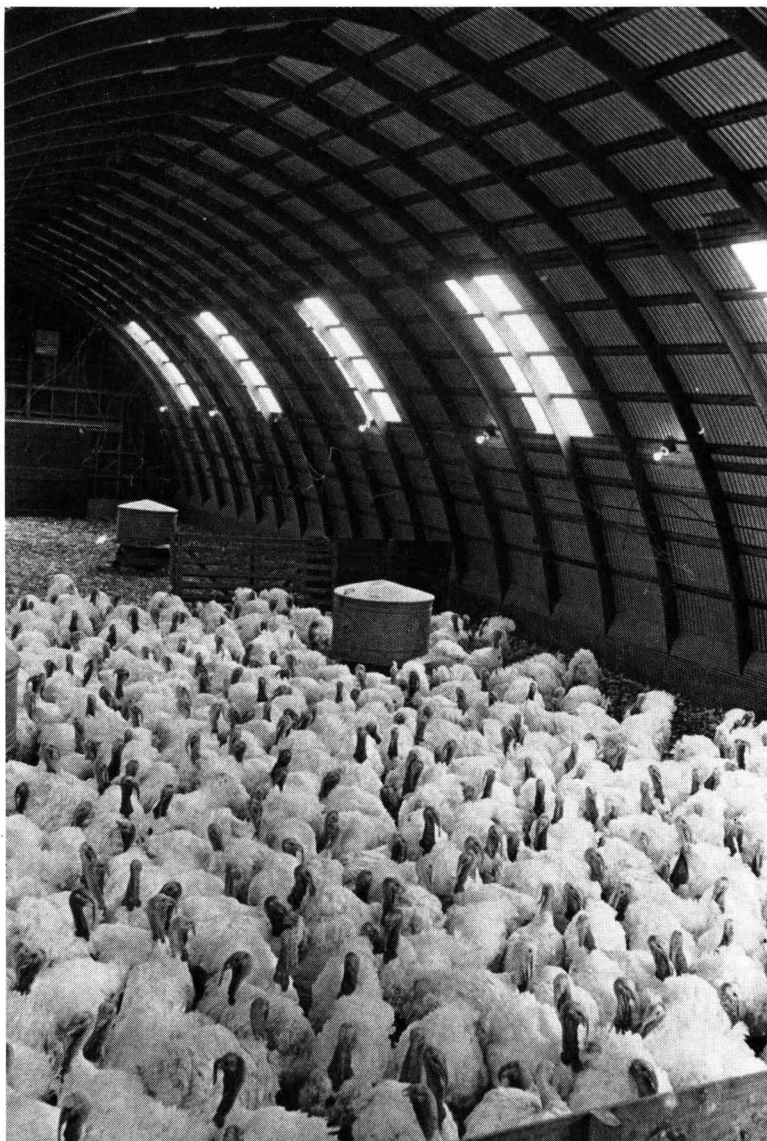
to either actual or potential contamination from radioactivity. However, some phosphate rocks used to produce fertilizer contain very low levels of radioactive uranium and thorium. Agriculture and forestry have suffered only minor adverse effects from this source of contamination.

- **Chemical air pollutants.** Crops, plants, and ornamentals are subjected to chronic injury in and near every metropolitan area. Livestock near mills

that produce steel, aluminum, and phosphate have been afflicted with fluorosis. In southern California, particularly, acute injury from chemical air pollution is widespread.

In the U.S. as a whole, losses to agriculture and forestry exceed \$500 million annually. Agriculture contributes only slightly to chemical air pollution in the form of hydrocarbons and smoke from burning crop residues in fields. On the other hand, major

***More big business.** A well-run automated poultry enterprise can care for 100,000 fowl—and in the process produce 5 tons of wastes daily. The wastes are not valuable enough to haul and spread as fertilizer. And when the wastes accumulate they emit offensive odors, afford breeding areas for flies and other vermin, and provide concentrated sources of pollution for surface and ground water*



forest fires produce tremendous quantities of smoke.

• **Airborne dusts.** An average of 30 million tons of natural dusts enter the atmosphere annually, most of it arising as soil blowing from inadequately protected fields under cultivation, deteriorated rangelands, and sand dunes. Not only is the land robbed of good topsoil, but a serious air pollution problem is created. However, progress is being made. The Kansas drought of the mid-1950's was just as bad as the Dust Bowl drought of the 1930's. But in the 1950's soil blowing was not nearly so serious. Another major source of airborne dust is industry—cotton gins, alfalfa mills, lime kilns, cement plants, smelters, and mining operations—which releases 17 million tons into the atmosphere annually.

• **Sediment.** Nearly 4 billion tons of sediment—primarily soils and mineral particles—are washed by storms into tributary streams in the U.S. each year. At least half comes from agricultural lands. Watershed research has shown that land cover is the major deterrent to sediment delivery. Improved technology in logging and construction of forest roads has reduced sediment delivery from forest operations. Research on the abatement of wild forest fires has made a major contribution in diminishing sediment delivery from forested lands. Soil loss from a burned area is often great.

• **Plant nutrients.** Plant nutrients enter surface water by the discharge of raw or treated sewage, some industrial wastes, and runoff and seepage from land. Barnyards and feedlots yield a wide variety of nutrients. Use of chemical fertilizers is suspected as being a significant source of plant nutrients found in streams and lakes. Detergents provide an abundance of soluble phosphate in sewage effluents. Much more information is needed on the role of plant nutrients in algal growth and eutrophication, and a variety of research projects on the subject are in progress.

• **Inorganic salts and minerals.** The quality of soils and waters is impaired by inorganic salts and minerals that come from natural deposits, acid mine drainage, industrial processes, and return flow from irrigated areas. The main problems created by inorganic salts and minerals occur when salt accumulates in irrigated soils and reduces

crop production. Of the 30 million acres of irrigated land in the 17 western states, about half have a potential problem with salinity.

• **Organic wastes.** These materials—forest trash, crop residues, sewage, animal wastes, food and fiber processing wastes—create the well-known and troublesome high biochemical oxygen demands (BOD) when they are carried in water. But on land the problem is no better, only of a different kind: they produce odors, are susceptible to fire, and attract flies and vermin. There are ways to use some of the contaminated water for agricultural purposes, but more research is needed on the effects of using such water on many crops. Also, much more data are needed on the relationship between low water flow and the level of water contamination.

logical effect of the plant species that produce allergenic pollen. There is little doubt of the ubiquitous occurrence of all these troublesome materials; the problem arises in mounting effective control programs for such pervasive materials.

• **Agricultural and industrial chemicals.** The discharge of synthetic organic chemicals such as detergents and pesticides has created environmental problems in our modern society. However, the benefits to agriculture far outweigh the damages, says Agriculture's report. Chlorinated hydrocarbons have caused considerable concern because of their persistence. Farming itself has suffered from the loss of honey bees and other beneficial insects through the consequences of pesticide vapors, and spray drift.



Dis-assembly line. Poultry processing also produces large quantities of oxygen-demanding wastes. In addition, these wastes make the water unsightly, unpalatable, and malodorous. More research needs to be done on such wastes to reduce quantities, improve treatment techniques, and possibly to develop useful products

• **Infectious agents and allergens.** Whether it be animal or plant disease agents or whether it be allergens alone, the fact is that soil, water, and air all serve as carriers for the agents or allergens that affect man, animals and plants. The control of such afflicting materials is possible, but only to a limited extent. Before reasonable control measures can be started we must first learn the source of the infectious agents and the distribution and physio-

• **Heat.** Agriculture and forestry contribute little heat to streams and lakes. Although heat does not have a major adverse effect on agriculture and forestry, the growing interest in providing recreational opportunities in rural and forested areas means fish and other aquatic life must be protected from heat pollution. Heat pollutes water in that the amount of oxygen water can hold in solution decreases with increasing temperature.

Reorganizing to Fight Urban Pollution

Mayor Lindsay's efforts to bring modern government to New York City include setting up a single agency to take a systematic and comprehensive look at environmental problems



Environmental Protection Administration's Eisenbud

No pollution tradeoffs for New York City

It's easy to think big when thinking of New York City—the nation's largest city and richest port, hub of business and cultural activities, site of the world's tallest building and of the United Nations headquarters. To that list, add pollution problems. Consider: its population of 7.8 million—which is topped by only a handful of states—is crammed into a 300 square mile area hemmed in by suburbs.

New York can't look to adjacent areas for amelioration of its problems, as Denver might with air pollution. In common with other cities, New York can look for help from improved technology and increased federal and state aid. New York can also look for help from Mayor John V. Lindsay's efforts to revitalize the city's government, which over the years had become so diffuse that it could hardly govern.

When Lindsay took over the city's reins in late 1966, the government was fragmented into something like 60 separate agencies. He drew up a plan that consolidates these 60 agencies into 10 super agencies, one of which is the Environmental Protection Administration (EPA).

On March 15, EPA took over the departments of sanitation, air pollution control, and water resources (itself a consolidation of activities formerly handled by four agencies). EPA thus becomes home to 19,500 municipal employees; its budget for fiscal 1968 totals \$409 million—\$184 million for operating expenditures, \$225 million for capital expenditures.

To run this big new operation, Lindsay reached out to New York University Medical Center's Institute of

Environmental Medicine. There he recruited Dr. Merrill Eisenbud, for the past nine years professor of environmental medicine and director of the Laboratory for Environmental Studies. Before that, Eisenbud had been with the Atomic Energy Commission for 15 years, most of it in the health and safety program. In his office in the Municipal Building, Eisenbud recently met with ES&T and discussed the major problems he sees facing his group and how he plans to cope with them.

Organizing efficiently

"Organized the way we are, we can take a systematic and comprehensive look at our environmental problems," Eisenbud believes. "I know of no other city that is organized this way. Even the Federal Government isn't—look at how its efforts are fragmented over many departments and agencies. Certainly, no administrative structure in itself is a panacea, but we feel we're in a better position to avoid trading off one form of pollution for another," Eisenbud declares.

He looks in his own backyard and sees a classic example of just such a tradeoff: "In 1951, the city started to require on-site incinerators in new construction to help the Sanitation Department with its growing problem of refuse collection. Now we have 17,000 of these incinerators and they're a major—and difficult to manage—contributor to our air pollution problem."

By consolidating agencies, the city should also be able to operate more efficiently. "Each of the three departments we took over had—to name just two examples—its own legal and payroll staffs. In many cases, where there used to be 30 people, we'll now have 10, so we can afford a higher level of administrative talent," Eisenbud points out.

"As we tried to staff EPA, we faced up to the same manpower crisis facing many American cities. In the Depression, civil service jobs were very desirable, so a lot of competent people signed on—and stayed on because they soon felt locked in by their pension rights. Many could have made 25%

more by going to the Federal Government," Eisenbud declares. "They're now retiring, and we've had to go out and recruit new people. Fortunately, Mayor Lindsay wants to upgrade the quality of our civil service. We have gotten off to a good start and have been able to attract some excellent new staff. Maybe they feel, as I do, that today's biggest challenges are in the cities."

Eisenbud is organizing EPA into three operating branches:

Department of Sanitation, with Capt. Griswold L. Moeller (USN, Ret.) as commissioner. A career Naval officer, he had considerable experience in manpower problems. The biggest of the three EPA departments, it employs 14,600 (most of them refuse collectors), maintains 4000 vehicles, and operates incinerators and land-fill sites. Its operating budget for 1968 is \$139 million.

Department of Water Resources, with Maurice Feldman as commissioner. He is a career engineer who started as a \$1000-a-year clerk with the Sanitation Department and worked his way up the ladder. He is assisted by chief engineer Martin Lang, who directs the Bureau of Water Pollution Control, and chief engineer Abe Groopman, who directs the Bureau of Water Supply. The Department of Water Resources supplies water and operates sewage treatment plants. It employs 4700 and has an operating budget for 1968 of \$43 million.

Department of Air Pollution Control, with Austin N. Heller as commissioner. Heller has been commissioner of this department for two years. For five years prior to that, he was with the Public Health Service. This department will be a sort of watchdog agency, maintaining surveillance on air pollution and probably noise abatement—which is just being set up. It employs 200 and has an operating budget for 1968 of \$1.8 million.

Eisenbud plans to consolidate some of the 15 laboratories of the Department of Water Resources. "This is a good example of the efficiencies we can realize with this type of organization. Commissioner Heller has operated an

excellent lab for the past two years, and so it's logical for him to head the water labs, too, since I have found many of them to be badly staffed. We'll also be able to make better use of some of the expensive new laboratory instruments."

Also helping direct the operations of EPA will be Mathias Spiegel as deputy administrator. "He is a lawyer who has been deputy city administrator for more than two years. Since I'm a novice in municipal government, I'll have to rely heavily on his experience," according to Eisenbud.

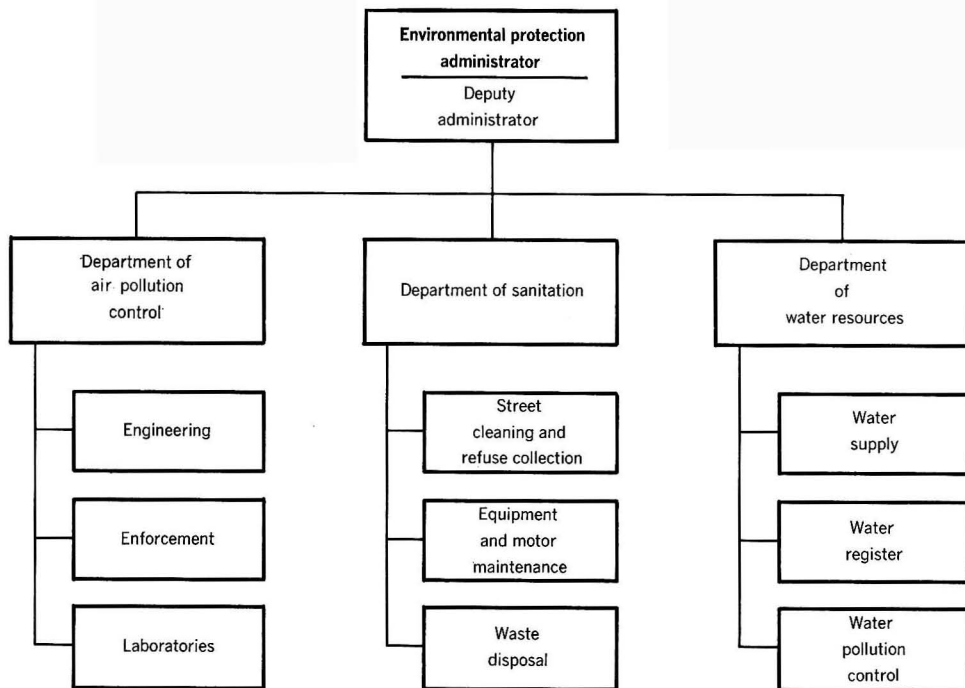
Facing immediate problems

With his basic organizational plan set and his staffing almost completed, Eisenbud is coming to grips with the immediate problems New York faces. As he sees them, they are: finding ways to get rid of solid wastes, building secondary treatment facilities to handle all sewage, and updating the city's obsolete enforcement procedures. This might well serve as an all-purpose list for cities, but the size of New York's problems tends to set them apart. Take the 5.8 million tons of refuse the city must dispose of annually. At present, it goes this way:

- 3.5 million tons to landfill.
- 2.3 million tons to incinerators.

The city has been fortunate as far as landfill sites are concerned. With so much water in its jurisdiction, it has been able to fill in many of its wetlands. Even in the 19th century it was filling, and today 17% of New York City's area is landfill.

But the end is in sight. According to the current schedule, available sites will be filled by the mid-1970's. Additional sites have been sought in Jamaica Bay, already filled in part. But conservationists protested—and properly so, in Eisenbud's opinion—pointing out that these are the last wetlands in the city. Wetlands serve as habitat for local and migratory wildlife and often for natural regulation of storm runoff. For the short term, Eisenbud will avoid using this wild area; however, for the long term, he is less sanguine: "Whether or not the city can



continue to afford this kind of a luxury forever, only time will tell."

Meanwhile, Eisenbud is applying systems analysis techniques to the problem of landfill. He would like to stretch out the life of the sites so as to take advantage of the new technology developing in incinerator design. For example, one design now being studied uses ultrahigh temperatures to produce a residue that could be dumped at sea—an obvious advantage to a city located where New York is.

One way to stretch out the sites would be to incinerate all wastes and use only the less bulky residue as fill. To do this, EPA would have to build several new incinerators—huge ones easily handling up to 5000 tons daily. It would like to locate them centrally to keep down the costs of moving the refuse about. The incinerators would be of advanced design and would be good neighbors, in Eisenbud's opinion. The first of these new incinerators will be built in the South Bronx, to be followed by a second unit in Brooklyn. The latter may be built at the old Navy Yard, where the heat could be sold to a nearby Consolidated Edison steam plant. The 11 incinerators the city now

operates are not, the city admits, particularly good neighbors. They handle about 7000 tons of refuse daily and in the process emit 40 tons of particulates—or 21% of the total particulate emissions. To bring this part of its operations up to standard, EPA ordered three prototype control devices—two electrostatic precipitators and a Venturi scrubber. In addition, it is undertaking a pilot project to test about six different control modules to develop the most effective air pollution control system for the changing nature of the city's refuse.

But EPA still has to contend with those 17,000 on-site incinerators, most of them in apartments. They are even worse air pollution offenders: in handling 3000 tons of refuse daily, they emit 30 tons of particulates—or 15% of the total emissions.

The city has come up with a flexible plan that permits each landlord to pick the refuse disposal method most economic for his building. Larger buildings will probably find it cheaper to upgrade their old incinerators with one of the 13 water scrubbers the city has approved for this purpose. They all use small amounts of water which is re-

circulated and cleaned up periodically. "We shouldn't end up with a pollution tradeoff this time," Eisenbud maintains.

The smaller building may choose the option of removing its incinerator and installing a compactor in its place. Refuse could still be dropped down the present chutes, then compacted to one third or one fourth. Compaction will facilitate collection, which accounts for about 80% of solid waste disposal costs. EPA has budgeted \$11.5 million this year to buy 500 new compaction trucks, which should also help the collection operation.

Ending untreated sewage

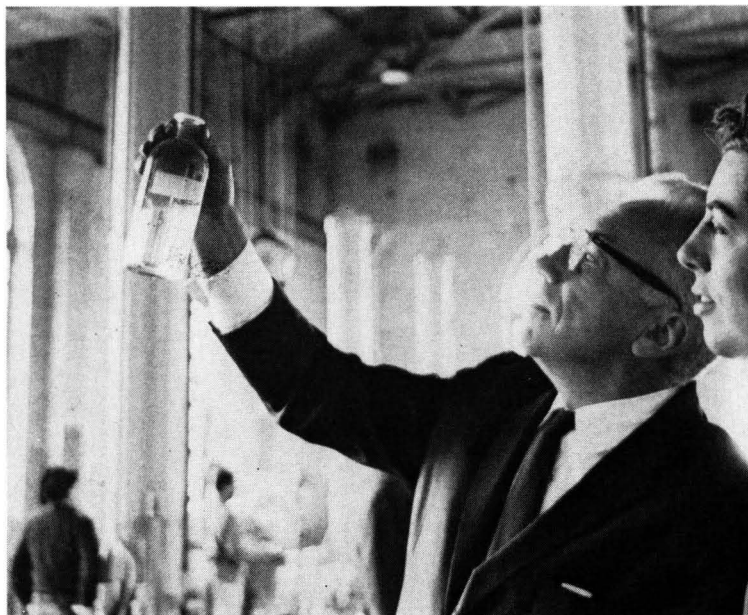
A second major problem facing EPA is building new facilities so that all of the city's sewage will receive biological treatment. About one third of the city's sewage does not receive such treatment; all along the west side of Manhattan, untreated sewage is dumped into the Hudson River.

The city now has 14 plants and needs four more to reach the goal of being able to treat 1.8 billion gallons per day by the mid-1970's. The plants

are designed for 70% removal. The plans for the first of the four plants aroused great public opposition. Designed to handle the liquid wastes of 1.5 million people—the population of Detroit—the plant is to be located on a 22-acre site at 141st Street on Manhattan's west side. A residential neighborhood on a high embankment will overlook the site, which is to be at water level.

The city called in an architectural firm to improve the appearance of the plant. It came up with a plan to install fountains on the roof of the plant and to surround it with a 15-acre landscaped park. The plan has been revised several times, with the final design not yet decided on. It may involve roofing over the entire plant and developing it as a 22-acre park with no fountains, but with a baseball diamond, fishing piers, and promenades. The changes will increase the cost of the plant from \$80 million to \$90 million. "We really need a radically new design for sewage treatment plants," Eisenbud says. "Current designs require great areas; few cities can spare such space for such a purpose."

Analyzing. *New York City's water resources department operates 15 laboratories, including this biological laboratory at Kensico. Eisenbud plans to consolidate some of the labs—an example of the kind of efficiencies he wants to achieve with the Environmental Protection Administration*

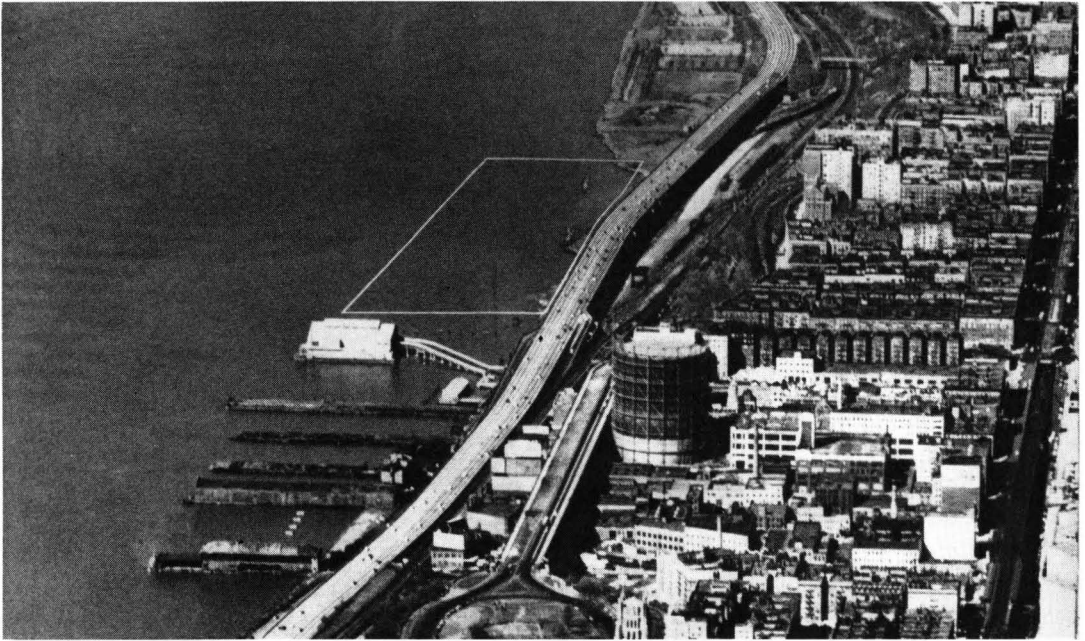


Inspecting. *Water leaving the Kensico Reservoir bound for New York City passes a high level inspection by Environmental Protection Administrator Merrill Eisenbud (left) and Robert D. Clark of his staff*

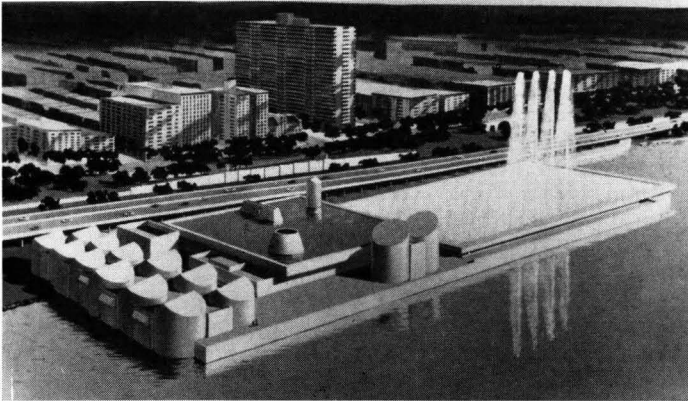
Updating enforcement procedures

Obsolete air and sanitation laws are a major reason New York City isn't a cleaner, pleasanter place, and Eisenbud wants to get some quick action on this score. He explains the problem this way: "We have a thousand inspectors on New York streets who can issue summons for violations on air and sanitation matters. They average less than one a week. Why? Because the procedures are impossible. For example, a sanitation inspector sees a store keeper is not keeping his sidewalks clean. First, the inspector has to write out a summons, describing the conditions in some detail. Then he has to present it to the responsible person—which can sometimes prove quite a job. Then both have to appear in court, tying the inspector up for a day. By then, so much time has elapsed that convictions are difficult."

Eisenbud has a task force looking into ways to streamline these procedures. One idea under consideration would arm inspectors with a Polaroid camera. A photograph of a violation could be witnessed by a passerby, then sent to a central office for handling. "We might even use this to enforce our alternate side of the street parking plan,

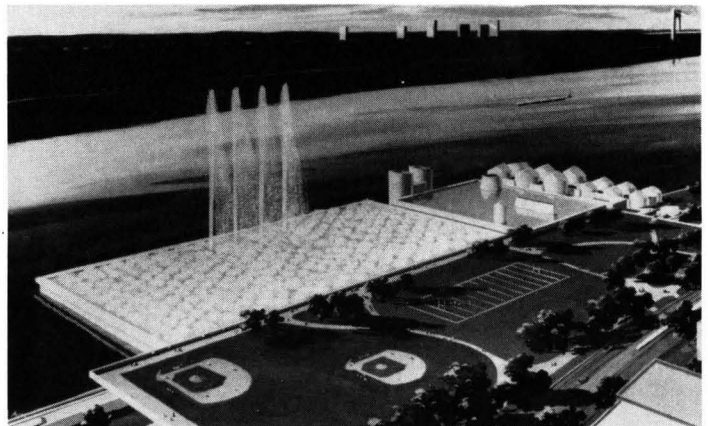


Beginning. *The first of the four big sewage treatment plants that New York City is planning will be located on this 22-acre site at 141st Street on Manhattan's west side (section outlined in white is proposed plant location)*



Objecting. *Residents overlooking the site objected at the prospect of so much brick and mortar so the design was changed to include some fountains*

Improving. *More changes were made in the design, this time to incorporate a park. The final plan has not been decided on, but may well involve roofing over the entire plant and making it into a 22-acre park (no fountains). In any event, new thinking must be brought to the design of such plants—the cities are just running out of space for such big plants, Eisenbud notes*



which we now have no way to enforce. The big street sweepers we use just can't maneuver around a car or two parked on the side of the street scheduled for sweeping. With modern data processing techniques, we can even collect unpaid fines when the owner registers his car," he believes.

"And," he goes on, "as people begin to get the idea that the city is going to be tougher, things will begin to shape up. We'll probably end up creating some new markets. I imagine it wouldn't be too long before someone came up with a mechanical sweeper that could sweep a sidewalk twice a day for a couple of dollars."

Tuning in on noise

The legislation that set EPA up also called for creation of a new program, one on noise abatement. A special task force of outside experts has completed a study of the problem. The group, headed by Neal Anderson, executive vice president of the New York Board of Trade, is similar to the air pollution task force of a couple of years ago, which was headed by Norman Cousins. The report, which is now at the printers, defines the city's noise problems and makes recommendations for dealing with them. EPA will develop its noise abatement program from this report.

When staffing is completed and programs are well underway, Eisenbud wants to begin to consider EPA's activities in bigger contexts—of regional planning and of long-term planning. He has on his desk now the Waste Management Report of the area's Second Regional Plan.

The report sketches the dimensions of the waste management problem for the New York region, a 2300 square mile area now inhabited by 19 million people. The report also looks at what effect these problems might have on the region by the year 2000, with its prospect of 30 million people. "Of course, we'll have to think more in regional terms—not just because environmental matters are basically regional, but because we have to if we want to participate in many federal grant programs," he points out.

"We are at a critical time in the development of cities," Eisenbud says. "Indeed, I feel the next few years will decide if cities can survive in their present form."



Swearing in. As part of his efforts to revitalize New York City's government, Mayor John V. Lindsay (right) consolidated 60 agencies into 10 super agencies. Here (above) Merrill Eisenbud is being sworn in as head of one of the super agencies, the Environmental Protection Administration. On the job, Eisenbud toured his new domain (below) visiting such facilities as the Delaware Aqueduct Aerator at Kensico, shown here



Stopping Oil Pollution of Nation's Waters Is a Chancy Affair

Domestic efforts to halt oil pollution of waters are growing and closely parallel cooperative international developments along the same lines

"Adequate means do not exist at present to protect the U. S. fully from the ecological disasters that can result from spills of oil or other similar hazardous substances." This warning is the principal message of the recent report to the President on oil pollution.

Prepared by the Secretaries of Interior and Transportation, the joint effort, "Oil Pollution, A Report to the President," is an assessment of the nation's legal administration and technological capabilities to cope with such spills. At best, pollution of the nation's waters by oil and other hazardous substances is controlled with varying degrees of success.

Nevertheless, preventive, remedial, and legal measures are being developed on the domestic scene, with ever increasing vigor, to protect our waters from these sources of pollution. Some of the domestic measures closely parallel developments on the international scene, especially the ones that concern oil spills in international coastal waters.

The report to the President covers not only oil spills from tankers such as the **Torrey Canyon** and **Ocean Eagle**, but also includes other important potential sources of oil pollution. The destructive characteristics of oil spilled in the environment were never better illustrated than when the **Torrey Canyon** ran aground, broke in two, and spilled much of the 119,000 tons of crude oil in her tanks into the sea.

However, the report is quick to note that tanker accidents are not the only source of oil pollution, and that attention must be given to the less spectacular but more persistent, more per-

vasive problems of deliberate and negligent oil spills.

Sources

Both water-borne and nonwater-borne sources of oil and other hazardous substances contribute to the pollution of the nation's waterways. Spills are unpredictable. Some are large, others are small; some are occasional, others are continual.

Although ships are but one of six significant oil pollution sources named in the recent report, they are, nonetheless, a prime pollution threat. For example, oil can be discharged from ships during the following operations:

- Cargo transfer and handling.
- Deballasting the vessel.
- Cleaning oil tanks.
- Pumping bilge waters (which usually contain waste oils).

Water-borne commercial fleets are powered almost exclusively by oil. About one vessel in every five is also engaged in transporting oil. In 1966, more than 50,000 medium size and large oceangoing vessels visited U.S. ports, carrying a cumulative volume of almost 300 million tons of potentially polluting material.

Domestic trade also transports substantial quantities of oil and related substances. In 1965, 80 million tons of such oil products were moved between American ports by coastwise tankers. In 1964, the 25,000-mile network of inland waterways was used to move 188 million tons of petroleum products and hazardous substances.

Also, tankers face the problem of tank cleaning. A 50,000 ton tanker may have 1200 barrels of oil to be cleaned from its tanks after unloading.

In 1963, prior to the development of the load-on-top procedure—which has proved successful in alleviating this problem—441,000 tons of petroleum were spilled overboard worldwide as a result of tank cleaning operations.

Nonwater-borne sources

There are four major nonwater-borne sources of oil pollution, according to the report:

- Waste oil from gasoline filling stations.
- Accidental spillage during industrial transfer and storage.
- Leaks from pipelines and related systems.
- Discharges from offshore mining operations.

The Corps of Engineers estimates that 40% of all oil pollution enforcement cases involve nonwater-borne discharges. Waste oil is but one example of this type of pollution. Close to 350 million gallons of used motor oil must be disposed of annually by more than 210,000 gasoline filling stations in this country, and these waste oils often wind up in city sewers. Although properly operated municipal facilities can normally cope with limited quantities of oil, the limit is easily exceeded.

Peter Spina, Executive Director of the New York State Petroleum Council, said that a statewide survey of this problem is being conducted in cooperation with the New York State Department of Health. According to Spina, the survey will attempt to quantify the extent of waste oil-caused pollution and to pinpoint areas within the state where substantial problems might arise.

Industrial transfer and storage is yet

another source of pollution. Both the quantities and varieties of oil and other hazardous substances transported and stored by industry are staggering. Almost 4 billion barrels of petroleum and natural gas liquids are used annually in the U. S. By 1980, the figure is expected to reach 6.5 billion barrels. Unfortunately, there is no readily available compilation of the number, size, and character of the facilities for moving and storing these materials.

Another source of pollution is pipelines. The U. S. is laced by about 200,000 miles of pipelines, which, in 1965, carried more than one billion tons of oil and other hazardous substances. The frequent occurrence of spills from accidental punctures and cracked welds in addition to leaks from corrosion illustrate the need for technical improvements in this area.

Offshore mining, also a major oil pollution source, contributes to pollution of offshore waters through the following operations:

- Blowouts of wells.
- Dumping of oil-based drilling muds and oil-soaked cuttings.
- Losses of oil in production, storage, and transportation.

- Rupture of pipelines by storms and the dragging of ships' anchors.

During the past three years, more than 50 sources of this type of pollution have been reported. And the problem is certain to get worse as the number of wells increases.

In the Gulf of Mexico, nearly 7000 wells have been sunk since 1960. These wells require more than 1800 miles of pipeline. At present, no charts which set forth the locations of all these structures are available to the mariner.

Preventive measures

The major effort in dealing with the oil pollution problem is in its prevention. Two important technical aspects are immediately evident. These are:

- Improvement in the design and construction of vessels.
- Improvement in the navigation of the vessels.

Present construction standards of vessels carrying oil and other hazardous substances are generally considered safe, according to the report to the President. Nevertheless, there is room for improvement.

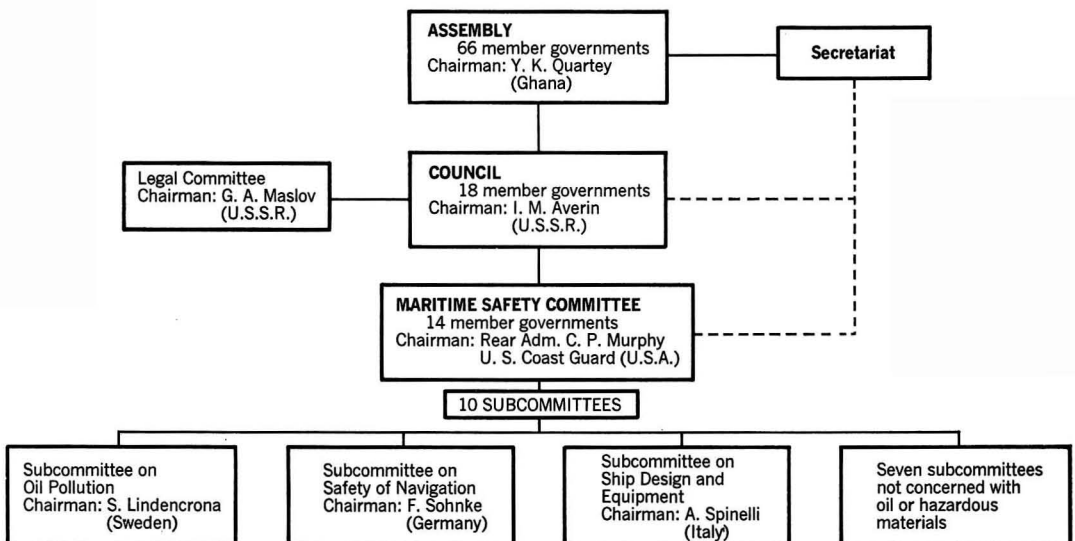
The question arises: Can these vessels be constructed to provide additional measures of protection against pollution? Quick, obvious answers are usually found to have certain drawbacks upon close examination. For example, the use of smaller vessels would minimize the pollution potential of a single serious accident, but the movement of any quantity of material would then require more vessels and more voyages. Consequently, the probability of accidents increases, along with the concomitant increase in navigational hazards.

Adding new devices

According to the report, research in design and construction should examine the feasibility of incorporating additional protective devices in the existing fleets. The report also suggests that research identify the balance between the cost of various design and construction standards and the degree of protection that these standards can be expected to provide.

Of immediate navigational concern is the safe movement of vessels in the heavily traveled areas near shore.

Intergovernmental maritime consultative organization



These areas include coastal waters, sounds, and harbor approaches.

Present U. S. regulations call for vessels to carry adequate and updated charts for their intended voyages. These regulations also require that an adequate number of experienced lookouts be posted on each vessel. They also provide for some supervision over the qualifications of personnel in the ocean and coastal service.

Still, there is room for improvement, since present U. S. regulations do not require vessels to carry sailing directions, Notices to Mariners, and tide tables. Steps must also be taken to increase the effectiveness of the U. S. Coast Guard Captains of the Port. The captains would provide port safety advisory information to vessels using U. S. ports. Vessels would have to contact the Captain of the Port for information concerning such details as location and availability of berth and anchorage, navigational hazards, harbor sanitation rules, and the like.

The use of recommended sealanes needs to be expanded to assure the most orderly movement of traffic in U. S. territorial waters and beyond. Already the U. S. has a background of experience in the subject. For example, according to the report to the President, recommended sealanes are used for the approaches to New York, the Delaware Bay, and the area of drilling platforms in the Gulf of Mexico. Studies have been completed for approaches to San Francisco, and still others are being considered for additional West Coast ports, and Boston, Norfolk, and Miami.

Through the Intergovernmental Maritime Consultative Organization, the U. S. will press for international adherence to upgrade standards in both ship construction and design and navigational improvements. Indeed, many recommendations calling for more stringent control are already included in the documents that are being forwarded for IMCO's November meeting.

Navigational research must examine the feasibility of some form of shore guidance system to promote safe movement of shipping. This research would concentrate on the practicability of such systems from the viewpoints of technical capabilities, costs, and anticipated improvements in marine safety records.

Cleanup

In spite of all preventive efforts, spills of oil or other hazardous substances will occur, either because of human error or calamities beyond human control. Present cleanup procedures leave much to be desired. They are often too expensive, too slow, too ineffective, and too destructive to the marine and land environment. Consequently, the need for the development of better cleanup procedures is critical.

The report points out that the nation's capabilities to cope with spills of oil and other hazardous substances are substantial, but relatively unorganized. However, recent progress in the development of contingency plans should obviate any such organizational deficiencies.

Assuming that a spill has occurred, has been noticed, and has been reported to the proper authorities, the critical point becomes one of an adequate cleanup strategy.

Contingency plans

Contingency plans must be developed, and their development is regarded as urgent. In a memorandum dated June 7, President Johnson asked the Secretary of Interior to assume the responsibility of developing multi-agency contingency plans which could be used in the event of oil spills emergencies. The memorandum was also sent to the Secretaries of Defense and Transportation and to the Director of the Office of Science and Technology.

The completed contingency plans, which are due on July 31, should cover all navigable waters, coastal waters, and waters of the territorial seas for the entire U.S.

The essential elements of these contingency plans, which begin with the discovery of an oil spill, are:

- Notification of proper authorities.
- Containment of spilled oil.
- Cleanup.
- Restoration.
- Disposal.
- Cost of the recovery.
- Enforcement activities.

The contingency plans being evolved at present contain all such facets of the mobilization scheme. It includes not only the various government and non-

government agencies to be notified and responsible individuals within each agency, but a priority for calling other persons within each agency. Efforts to contact each agency noted in the contingency plan would be continued until contact had been established.

The contingency plans would further specify setting up an operations center in the vicinity of the spill to serve as the focal point for all activities associated with the cleanup. The center would operate in decision making, reporting, and other communicating activities involving the spill. More importantly, the center would be the operations point for implementing the action plan of cleanup.

Action sites—places where men and materials can counteract the effects of the spill—would also be outlined in the contingency plan. These preselected sites would be readily accessible and would have various monitoring and other control activities for reducing or eliminating the effects of the spilled materials.

Combative materials for oil

In any emergency situation, rapid mobilization is imperative. Sources of these materials, from chemicals to naturally occurring combatives such as straw, must be available at a moment's notice.

Sources of equipment as well as manpower would also be enumerated in the plans. Both quantities and locations of resources must be determined in advance of any emergency condition. Thus, a listing of addresses and



Miller: U. S. delegate to IMCO
Considerable cooperation

Cooperation in international maritime matters promoted by U.N.

The Intergovernmental Maritime Consultative Organization (IMCO), a specialized agency of the United Nations, provides machinery for international cooperation in shipping matters. Its membership comprises 66 nations, including all of the major shipping nations of the world. Its current position on oil tanker casualties in international coastal waters covers 18 study items of a preventive, remedial, or legalistic nature to deal more adequately with the continuing threat of oil spills.

After the **Torrey Canyon** disaster (March 18, 1967) and at the request of the British government, the council of IMCO, its administrative body, held a special meeting (May, 1967) to organize a review of the problems related to the transportation of oil or other noxious or hazardous cargo. The major part of that meeting was devoted to a review of specific measures to prevent future oil pollution accidents and to mitigate the damage from such pollution. Each proposal put forth in the British statement of the **Torrey Canyon** disaster was refined, discussed, and then assigned by the council to the Maritime Safety Committee and a legal committee. In turn, MSC called on three of its subcommittees to study the problem.

Following the council's meeting, the three subcommittees and the legal committee of IMCO have been discussing these study items at their meetings—usually scheduled at intervals of four or five months—and are slowly coming to grips with the problems. Although the work is far from complete, consensus on these study items will be presented at IMCO's extraordinary session of the assembly, scheduled for November 25–29 at IMCO headquarters (London, Eng.) to deal specifically with the oil pollution problem.

Present consensus on these important study items is not likely to change appreciably before the November meeting. For the meeting, only measures of a preventive nature are being forwarded. These measures include 15 draft resolutions and three proposed amendments to the International Convention for Safety of Life at Sea, 1960. At present, no resolution or amendment is in order for the International Convention for the Prevention of Pollution of the Seas by Oil, 1954, as amended 1962.

At some future date, recommendations of both remedial and legalistic natures will be forwarded as the work of the various subcommittees and the legal committee nears completion.

IMCO is the forum

Prior to the May meeting, Rep. Edward A. Garmatz (D.-Md.) chairman of the House Committee on Merchant Marine and Fisheries, stressed the importance of IMCO as the appropriate agent to lay down a framework for international cooperation. The U. S. supported the British request for the special IMCO council meeting and sent its delegation to that meeting. The U. S. delegation, headed by William K. Miller, Director of the Office of Maritime Affairs in the Department of State, also included three congressmen.

According to Miller, IMCO operates at a funding level of about \$1 million per year, making it one of the lowest funded organizations of the U. N. Nevertheless, there is considerable cooperation among member governments and each member government's share of the funding is based primarily on tonnage of its fleet, Miller noted. The U. S. share is 10% of the total, he added.

Organization

IMCO is the first international organization concerned solely with maritime affairs, according to Comdr. L. W. Goddu, Jr., Chief, International Affairs Division of the U. S. Coast Guard.

The purpose of IMCO is to achieve the highest practicable standards of maritime safety and efficient navigation by facilitating cooperation among member governments in all kinds of technical matters affecting shipping. On the average, IMCO schedules a total of 28 business meetings each year at its London headquarters.

IMCO is composed of three main bodies—the Assembly, the Council, and the Maritime Safety Committee. In addition, a Secretariat, a group of international civil servants, keeps IMCO functioning on a daily basis.

- The Assembly, the main body of IMCO, is composed of the 66 member nations. Any action taken by IMCO must be approved by the assembly.

- The Maritime Safety Committee handles all technical matters and handles nontechnical matters.

- The Council of IMCO comprises 18 member governments for IMCO and meets twice every year. MSC lists 14 member governments but will probably expand to 16 at the November meeting.

MSC is further divided into 10 subcommittees of technical experts. Three of the subcommittees are actively involved with corrective measures to reduce the oil pollution threat.

In addition, a legal committee apprises the council on problems of international law.

Subcommittee on safety of navigation

Preventive measures to eliminate beforehand some of the hazards of oil transportation occupy the attention of the subcommittee on safety of navigation. Under the chairmanship of F. Sohnke of Germany, this subcommittee is concerned with the following:

- Sealanes.
- Navigational equipment.
- Shore guidance.
- Speed restrictions.
- Periodic testing of equipment.
- Training of officers and crew.
- Use of the automatic pilot.
- Identification and charting of hazards.
- Reinforcement of lookout systems.

This subcommittee should complete its work by November, in time for the London meeting. Indeed, many of the documents that are being forwarded for that meeting stem from this subcommittee's activities.

Subcommittee on ship design and equipment

The newly formed subcommittee on ship design and equipment held its first meeting in January. Special attention centers on the adequacy of braking equipment on large tankers, such as those of the 300,000 deadweight ton class, according to chairman Spinelli of Italy.

A plan to control the design, construction, and equipment of ships above a certain size carrying oil or other hazardous cargo is also being considered. If such a proposal is approved, an amendment to the International Convention for the Safety of Life at Sea would probably be introduced at a later date.

Subcommittee on oil pollution

Remedial measures designed to limit or mitigate damage from from the oil pollution accidents are being studied by the subcommittee on oil pollution. Headed by S. Lindencrona of Sweden, this subcommittee divides its responsibilities as follows:

- Procedures in the event of accidents.
- Research on oil clearance.

Regional or interregional contingency plans must be formulated and are the first order of priority of the subcommittee. Member governments need to establish standard operating procedures so that each can cooperate with the others on short notice to provide manpower, supplies, equipment, and scientific advice to deal with discharge of oil or other hazardous substances, according to Lindencrona.

Precedents already exist for regional cooperation among countries for handling oil tanker casualties. The German delegate of the subcommittee pointed out that West Germany

cooperates with other nations bordering on the North Sea whenever a pollution hazard appears. During the **Torrey Canyon** incident, England and France also set up joint patrols to watch the direction of the oil slicks.

Because great danger exists to fish resources from the present methods of dealing with pollution, research concentrates on the following items:

- Containment of oil pollution by mechanical, scientific, or other devices.
- Methods to destroy the polluting agents without damage to valuable plant or animal marine life.

The subcommittee on oil pollution probably will not complete its work before late 1969.

Legal committee

The tangle of legalistic measures is being considered by IMCO's newly established legal committee, headed by G. A. Maslov of the U.S.S.R. Prior to the committee's establishment, the only international organization experienced in handling maritime legal problems was the *Comité Maritime Internationale* (CMI), a private nongovernmental group of international lawyers which meets periodically in Brussels. IMCO's new legal committee will draw on the CMI on a consultative basis, as needed, and then present an opinion to members governments of IMCO.

The legalistic study items relate to changes in international law. Measures are designed to extend the rights of coastal states endangered by a pollution accident, and also to assure compensation to parties injured by such an incident. These measures include:

- Legal rights of a coastal state. International law does not adequately take into account the rights of countries which may have no direct interest in a ship or its cargo but whose territory may be affected by an accident to the ship.
- Official inquiry. Can a coastal state affected by an accident on the high seas participate in the investigation by the government of the vessel's flag?
- Liability in event of accidents. Should the owners or operators accept liability, independent of negligence, to cover damages arising out of pollution caused by an accident?
- Compulsory insurance for tankers. Is this a feasible approach?
- Movement of salvage equipment. Some countries do not allow equipment from other nations to enter their waters for salvage operations.

Because the number of these problems will increase in coming years, the work of the legal committee will probably continue to increase.

Growing problem

Oil tankers account for about 40% of the world's ocean-going traffic today. Both the number and size of these tankers are increasing. Japanese yards are scheduled to build six tankers, each of more than 300,000 deadweight ton capacity. All six will be chartered by Gulf Oil.

At the recent 13th annual Tanker Conference (Williamsburg, Va.) sponsored by the American Petroleum Institute, John G. Robinson, technical director of Shell International Marine, Ltd., said that this company saw neither the need nor the economic wisdom of going beyond the 200,000 deadweight ton capacity in new tankers. The economic advantage of tankers larger than 200,000 tons capacity was marginal, he added. This advantage could be offset altogether by inflexibility of operation and the need for additional investments to upgrade shore facilities to accommodate them. Another problem is the increasing draft of these new tankers, a factor that navigational charts do not take into account.

Lesson learned

The principal lesson of the **Torrey Canyon** disaster—one of the major ship disasters in maritime history—is that the potential danger is too great and available remedies are too difficult, unsure, or expensive to permit reliance on measures that are effective only after the oil is on the water.

A board of investigators, appointed by the Liberian government, reported that the **Torrey Canyon** accident was not caused by any mechanical failure but was solely the result of human error. The board recommended that License No. 21127, issued by the Republic of Liberia to Pestrengo Rugiati, master of the **Torrey Canyon**, be revoked. The board considered that this disaster demonstrated the desirability of international agreement to establish recommended sealanes or routes near coastal areas.

The May meeting was called solely to deal with the problem of tanker casualties in international coastal waters. It was not intended to inquire into the problem of pollution caused by routine cleaning and dumping of oil by tankers. Thus, any improvements that may result in this area will be incidental to the main objective.

Emergency authority

During the first 48 hours of the **Torrey Canyon** disaster, nobody was sure that the British government had the authority to act. To prevent such a U. S. dilemma, H. R. 8006 and its companion bill, S. 1586, have been introduced. These bills would authorize the President to take emergency action to prevent or limit pollution of our coastal waters and beaches in the event of a tanker casualty near our shores. No action has been taken or scheduled on these bills or any of 13 other House bills on the subject.

Comdr. Goddu explains that both IMCO resolutions and recommendations require a majority vote of the assembly for approval. To amend these two international conventions, approval must first be received from two-thirds vote of the assembly. Following approval by the assembly, the secretariat distributes amendments to any international convention to each of the contracting governments of the convention. Now, 69 contracting governments, not necessarily IMCO member governments, are members to the International Convention for the Safety of Life at Sea, 1960. Also, 38 contracting governments are members to the International Convention for the Prevention of Pollution of the Seas by Oil, 1954, as amended in 1962.

The secretariat requests notification when the amendment has been ratified by contracting governments. When the IMCO assembly receives ratification from two thirds of its member governments the assembly advises and encourages all IMCO member governments to adopt the resolution, recommendation, or amendment at once. In any event, the item becomes effective one year subsequent to the date of two-thirds approval.

Accomplishments

IMCO's most recent accomplishment is the upgrading of fire protection standards on passenger vessels. The IMCO assembly has approved amendments to the International Convention for the Safety of Life at Sea, 1960. These amendments are directed at:

- Upgrading existing passenger ships.
 - Establishing new regulations for future passenger ships.
- Following the loss of the **Lakonia** and 125 of its passengers by fire during a Christmas vacation cruise in December, 1963, and the **Yarmouth Castle** by fire in November, 1965, the U. S. pressed for immediate action to guard against shipboard fires. The present amendments are the direct result of IMCO's Maritime Safety Commission continuing activity. These amendments further confirm that IMCO is the forum for handling international maritime problems.

Now, the amendments must be accepted by two thirds of the 69 contracting governments to SOLAS, 1960. Inasmuch as formal ratification of the amendments takes considerable time, the assembly invited all these governments not only to accept the amendments at the earliest possible date, but actually to put them into effect as soon as possible. To date, 16 contracting governments, including the U. S., have indicated their ratifications to IMCO.

telephone numbers of companies, suppliers of equipment, and manpower reserves will probably be contained in the plan.

An important item related to oil spills is the availability of oil storage facilities. After oil is recovered from the waterway it must be transported and stored. All these considerations must be included in the development of any successful plan.

Cost

A comparison between the cost of preventive measures and the cost of cleanup and damages is not susceptible to precise cost-benefit analysis. The cleanup cost for recent spills has varied from less than \$1000 (for straw to absorb a small quantity of oil spilled in an inland waterway) to more than \$8 million (in damages that the British Government is trying to recover from the owners of the **Torrey Canyon**). The \$8 million figure does not include the cost to local governments and private agencies in England, nor does it take into account the extensive efforts made by the French on their coast. Nor does the figure cover the damage to the natural and recreational resources of either England or France. Recent estimates put the total cost of damages from the **Torrey Canyon** incident at \$13-\$15 million.

However, the report to the President notes that the effect of a major pollution episode on any particular recreation region is not difficult to estimate. For example, a serious spill along the Long Island shore during summer months could mean that 20 million

people-visits (people times visits) would be lost. Assuming an economic loss of \$1.50 per lost visit, the immediate loss would be \$30 million. A serious spill in the Los Angeles region could cause the loss of 34 million people-visits. On the same basis the cost to the Los Angeles region would come to \$51 million. The report is quick to point out that these costs are quite separate from other indirect costs such as the value of lost oil, cost of cleanup, or the economic damage to wildlife resources.

Legal measures

The Oil Pollution and Hazardous Substances Control Act of 1968, the proposed legislation for the control of oil spills and spills of other hazardous substances on the domestic scene, would cover disasters such as the **Torrey Canyon** incident, and the day-to-day discharge of these contaminating materials into the nation's waters. This proposal amends the Federal Water Pollution Control Act (as amended) and the Oil Pollution Act of 1924. Basically, the proposed legislation, S. 2760 and H. R. 15906, expands present legislation and covers the following additional points:

- Extends the prohibited area for spills.
- Includes shore facilities for the first time.
- Provides for cleanup.
- Specifies other hazardous substances.
- Makes owners liable for the full cost of cleanup rather than limiting the cost to the salvage value of the vessel.

Discharge of oil is prohibited from vessels in waters within 12 miles of shore, which includes both the 3-mile territorial and the 9-mile contiguous zones.

In 1958, the Convention on the Territorial Sea and the Contiguous Zone permitted the U. S. to exercise, within a 9-mile zone contiguous to its territorial sea, the control necessary to prevent the infringement of its "sanitary regulations within its territory or territorial sea." Nevertheless, a problem may arise in this regard, since certain important maritime nations—for example, Greece, Japan, Norway, Sweden, and France—are not signatories to this convention.

For the first time, shore facilities are prohibited from discharging oil into their shoreside waters. Also significant in the proposed legislation is deletion of the wording "gross negligence" from the Oil Pollution Act of 1924. Proof of gross negligence is a difficult task in any court. However, if the owners of a vessel fail to clean up an oil spill caused by that vessel, the Department of Interior would be empowered to do so. The full cost incurred by the Interior would be levied on the vessel's owners. The proposed legislation authorizes a revolving fund in the U. S. Treasury to be used by the Secretary of Interior to carry out cleanup operations.

Furthermore, the coverage of the oil pollution provisions is extended to Puerto Rico, Guam, American Samoa, and the Virgin Islands. Had this legislation been in effect during the recent **Ocean Eagle** spill, funds would have

IMCO's consensus on items of study

SUBCOMMITTEE ON OIL POLLUTION

Chairman: S. Lindencrona — Sweden

Study items

Regional or interregional contingency plans

- Recommends that member governments encourage the development of national and regional contingency plans to deal with major spillages of oil or other noxious or hazardous cargo.
- Recommends that member governments intensify research into the various aspects of oil pollution prevention.
- Encourages member governments to strengthen detection and enforcement provisions, as well as the penalties and oil record book.
- Recommends special circumstances when oil may be discharged into the sea instead of into oil reception facilities.
- May propose, at a later date, changes in the definition of "oily mixture" and the provisions allowing the discharge of oil into the sea.
- May propose, at a later date, amendments to the prohibited zones.

Continuation and intensification of research

Possible amendments to the International Convention for the Prevention of Pollution of the Sea by Oil, 1954, as amended 1962

SUBCOMMITTEE ON SHIP DESIGN AND EQUIPMENT

Chairman: A. Spinelli — Italy

Study items

Control of design, construction, and equipment aspects

- Expects no action on this topic. No proposals have been formulated. Possible changes to the International Convention for the Safety of Life at Sea will be forthcoming.

LEGAL COMMITTEE

Chairman: G. A. Maslov — U.S.S.R.

Study items

Affected state's ability to participate in any official inquiry

- Recommends that representatives of an affected state be permitted to participate in any official investigation.
- Plans to sponsor a special IMCO conference to develop a new international convention.
- Present stage of discussions does not allow for any action at this time.
- Present stage of discussion does not allow for any action at this time.
- Recommends at most that member governments allow foreign based seaborne salvage equipment access to their territorial waters.

Measures which a state may take to protect its shoreline

Liability of owners or operators for damages to third party
Surveillance and control of coastal state

Access of seaborne salvage equipment of other flags into territorial waters

SUBCOMMITTEE ON SAFETY OF NAVIGATION

Chairman: F. Sohnke — Germany

Study items

Sealanes

- Plans to distribute information regarding approved traffic separation schemes and areas to be avoided.
- Recommends that member governments adhere to the specified routes.
- The International Convention for Safety of Life at Sea, 1960, will probably be amended.
- Vessels more than 1600 gross tons will be required to carry an approved radar and a gyro compass.
- Vessels more than 5000 gross tons will be required to carry an echo-sounding device.
- Electronic position fixing equipment will be required on all ships carrying oil or other noxious or hazardous cargo.

Shipborne navigational aids

- Recommends that member governments set up advisory services in ports that warrant it by the importance and nature of their traffic.
- Recommends use of organized pilot services where their use could enhance safety of navigation.
- Will probably define vessels or class of vessels for which embarkation of a pilot would be mandatory.

Guidance of ships from shore-based stations and port advisory services

- Recommends that ships have available on the bridge the necessary information regarding the maneuvering capabilities of the particular ship and stopping distances under various draft and speed conditions.

Restriction of speed and maneuvering capabilities of the ship

- Urges member governments to ensure that navigational equipment is used effectively and tested at sea as frequently as possible. These tests should be recorded in the logbook.

Periodic testing of shipborne navigational equipment

- Possibility exists that a joint IMCO-International Labor Organization recommendation may be put forth.

International standards of training and qualifications of officers and crew

- Proposes that a new regulation be added to Chapter V of SOLAS 60. Where the automatic pilot is used, it should be possible to establish immediate control of the ship's movement.

Use of the automatic pilot

- Proposes that a new regulation be added to Chapter V of SOLAS 60 to ensure that all ships carry appropriate navigational charts and publications for the intended voyage.

Charting of routes and adequacy of charts and publications

- Expects no action on this topic.

Reinforcement of lookout system



IMCO's symbol

been immediately available for clean-up of the oil.

Criticism of proposed legislation

At recent hearings before the House Committee on Public Works, several criticisms were levelled at the proposed legislation. So, there seems little doubt that amendments will be introduced before the bill is reported. For example:

- The proposal does not include provisions for controlling the release of used motor vehicle oil into the nation's waterways.

- No provision is made for settlement of jurisdictional disputes in clean-up operations. According to the proposed legislation the Department of Interior would have responsibility for clean-up. In the **Torrey Canyon** disaster, 48 hours transpired before the British Government took responsibility for the spill and moved in to effect the clean-up.

More research

Myriad R&D programs are recommended in recent reports on oil pollution. A recent literature survey on the subject—prepared by Battelle-Northwest for the Department of Transportation and the U. S. Coast Guard—specified no less than 73 recommendations for R&D. R&D on these problems is never ending. So, as new, improved, and economically feasible methods become available, they will be incorporated into the contingency plans.

Hal Bernard of FWPCA says that the total FWPCA R&D program for fiscal 1968 was \$28 million. Of this total, \$1 million was devoted to oil pollution. FWPCA issued an RFP (request for proposal) to elicit R&D programs on which companies might be willing to work. More than 200 RFP's were received. Thus, FWPCA plans a serious examination to evaluate their current program.

In-house laboratory

FWPCA's expertise in the handling and transporting of hazardous cargoes is being developed at the agency's laboratory (Edison, N. J.). This laboratory will serve as an information center and repository of information, and will also be responsible for continuous updating of technological advances for prevention, control, restoration, and advice pertinent to oil pollution.

Research needs

Research will examine the following items:

- Methods for making natural products more capable of tying up oil. For example, no straw was easily available to adsorb any of the oil in the **Ocean Eagle** spill, Biglane explained. Instead, bagasse, the waste pulp from the stalks of sugar cane which are subsequently used in the manufacture of paper, was tried with no apparent success. Hence, the need for having naturally occurring products indigenous to the scene of the spill available for oil absorption means that techniques must be developed to appropriately modify such natural products as sawdust, dry canner wastes, ground bark, seaweed, and the like.

Another research area involves tagging procedures for oil cargoes. The technology for nonradioactive tagging of such cargoes is available today, according to Rademacher. This tagging procedure would permit the Department of Interior to track down an otherwise unidentified polluter after he leaves the scene of the spill.

Improved methods for cleaning oil-soaked birds are included in the list of FWPCA research priorities. Also, skimmer devices with increased pumping capacities are sorely needed. Coraling devices such as booms and the like must be improved so that they can handle other than quiet harbor type operations.

One research program, currently funded by FWPCA R&D grants, involves the use of a pneumatic curtain of air to protect bathing beaches from pollution. According to a spokesman of American Machine & Foundry, Inc., this program will demonstrate the effectiveness of enclosing a bathing area with a dense curtain of air bubbles released from perforated pipes on the bottom of the area. Theoretically, the circulation pattern of water, caused by the rising bubbles, will set up a barrier for flotsam, oil, and the like.

Federal Policy and Environmental Chemistry

The success of evolving federal policy in restoring and maintaining an optimum environment depends on the ingenuity and success of chemists to provide an adequate scientific and engineering base

The chemical industry is viewed as a major contributor to pollution because the contaminants in the environment are, after all, chemicals, and because a great many sources of pollution are within the industry. Pollutants react with human health or property values in a chemical way, whether their source be a community sewage treatment plant, a private automobile, or an industry quite separate from conventional chemical manufacture. Thus, for a variety of reasons, chemical science and engineering have been placed on the defensive.

But as we understand more of the complex nature of pollution—waste management gone wrong—in a highly technical society, the other side of the coin is revealed. This aspect of chemistry shows the profession to be the means by which we can restore and maintain environmental quality. This article reviews federal policies, shows their dependence on science, and illustrates the constructive role for chemists and the industry—a role that is essential if federal policy for pollution abatement is to succeed.

Traditional ways no longer will do

Pollution abatement depends on many factors—economics, social institutions, public opinion, legal procedures, political judgments, and technology. The best scientific understanding of the problem will be useless without the means of implementing the knowledge. It is equally true that all

This article is based on a paper presented at the 155th ACS National Meeting in San Francisco, Calif., March 31–April 5, 1968

the weight of public opinion will not prevail unless the technology for abatement is adequate and effective. The chemical community gets involved because the information for improved management decisions is largely chemical in nature.

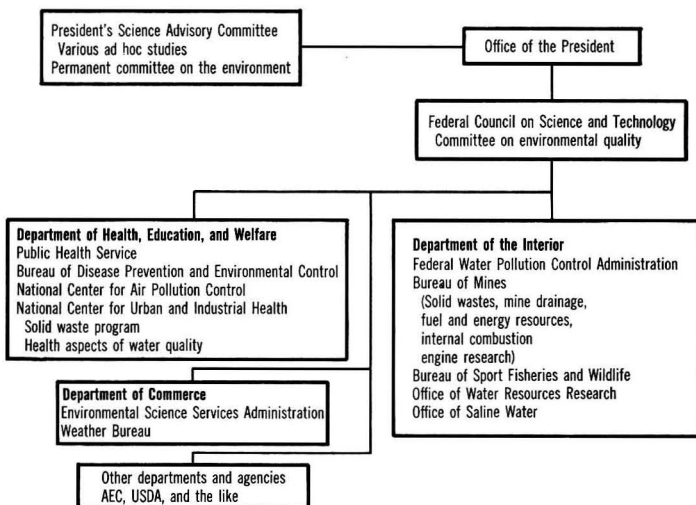
A number of changes have taken place in the world recently which make it impossible for us to continue formerly or traditionally accepted practices. First, there is no longer any place to put the materials which society rejects. The population of the world is so distributed that no convenient dumping grounds, or streams, or air masses exist which are not also the natural resources of other persons.

The environment probably does have a limited assimilative capacity, but the polluter cannot use it up himself without infringing on the rights of the next user.

The second distinctive change is that man has greater powers to disrupt the environment than ever before. Radioactive materials and physiologically active chemicals are long-lived and spread throughout the biosphere. Effects which cannot be predicted may be profound and irreversible. Mistakes may be expensive and difficult to correct, once they are discovered.

Third, the conservation of resources must lead to a recycle economy instead of the present "use and discard"

Executive branch organization for environmental quality



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philosophy. None of our raw materials, save sunlight, is limitless. Pollution runs contrary to good conservation science because of the second law of thermodynamics. When a material is contaminated or widely dispersed, it becomes that much more difficult to include in a recycle system. Since we must indeed use the environment heavily to support our standard of living and extend it to developing nations, a high quality environment is synonymous with efficient management.

Finally, the laws of genetics suggest that man cannot adapt to an environment drastically different from that in which he evolved. Even if we would

agree to accept some of the changes in environmental values our civilization has brought on, we could not physically accommodate to them. So, preservation of a reasonably normal and stable environment is urgent and necessary. Waste management must remain under close control and be supported with adequate knowledge of human ecology.

Development of federal legislation

The Federal Government's involvement in environmental quality stems from a number of historical roots, among them being the Constitutional mandates to promote the general welfare and to regulate commerce. The

Federal Government is responsible for public health; it is the only government which the citizen can turn to when lesser jurisdictions disagree, and it is the logical supporter of research and development of nationwide relevance and application.

Water pollution legislation originated in the Rivers and Harbors Act of 1899, which prohibited debris in the interests of navigation. The Public Health Service Act of 1912 concerned waterborne diseases, and the Oil Pollution Act of 1924 was designed to prevent discharges into navigable waters that would damage aquatic life, recreational facilities, and harbor installations. After a temporary act in 1948, the Federal Water Pollution Control Act of 1956 was passed; it called for states to set standards and gave enforcement authority to the Federal Government if local efforts failed. Finally, a systems approach to water pollution abatement was authorized in the Clean Waters Restoration Act of 1966.

Air pollution legislation has followed a similar path. The 1955 Air Pollution Act was a small program of research and technical assistance to local control districts. It is worth noting that the intense problem of Los Angeles had motivated almost all the scientific work done to that date. The Clean Air Act of 1963 is very similar to the Federal Water Pollution Control Act. Amendments in 1965 and 1966 have added funds and specific research tasks. The Air Quality Act of 1967 completed the federal legislation by calling for state and regional standards to be enforced locally, if possible.

Legislative branch organization for environmental quality

Senate committees	House of Representatives committees
<p><i>Appropriations</i></p> <ul style="list-style-type: none"> Interior and related agencies Public works Labor, HEW, and related agencies <p><i>Commerce</i></p> <ul style="list-style-type: none"> Merchant marine and fisheries <p><i>Interior and insular affairs</i></p> <ul style="list-style-type: none"> Minerals, materials, and fuels Water and power resources <p><i>Labor and public welfare</i></p> <ul style="list-style-type: none"> Health <p><i>Public works</i></p> <ul style="list-style-type: none"> Air and water pollution <p><i>(Others: agriculture, government operations, and the like)</i></p>	<p><i>Appropriations</i></p> <ul style="list-style-type: none"> Interior and related agencies Labor and HEW Public works <p><i>Government operations</i></p> <ul style="list-style-type: none"> Natural resources and power <p><i>Interstate and foreign commerce</i></p> <ul style="list-style-type: none"> Public health and welfare <p><i>Merchant marine and fisheries</i></p> <ul style="list-style-type: none"> Fisheries and wildlife conservation <p><i>Public works</i></p> <ul style="list-style-type: none"> Rivers and harbors <p><i>Science and astronautics</i></p> <ul style="list-style-type: none"> Science, research, and development <p><i>(Others: agriculture, interior, and the like)</i></p>

Federal abatement enforcement is the ultimate weapon to assure both air and water quality.

This legislative history shows that the basic policy of the government is cautious except where direct hazard to human health is involved. The first federal activity is monitoring and analysis of the environment to define pollutants, their concentration, and sources. Local governments are aided by the Federal Government in staffing and equipping offices and agencies that are charged with learning just what the problem is in the local areas. The techniques are developed under federal research grants because they are widely applicable.

Gross and obvious pollutants

As soon as knowledge about pollutants begins to accumulate, there is a tendency to leapfrog immediately into an abatement plan. In the case of gross and obvious contamination, this is justifiable and often works. Strong emotional demands for a less dirty city motivated smoke elimination in Pittsburgh and St. Louis. The technology for particulate collection and combustion control was adequate. Therefore, no refinement of the cause and effect relationships was requested. Another example is the acceptance of primary sewage treatment as the minimum which any water user must perform before the effluent goes to a receiving water.

These types of pollution are the result of contaminants which are in a different physical state (or phase) from the environment in which they are carried. That is why the average citizen sees them and recognizes them as problems. It is also why they are usually cheaply and easily removed. The remedies for particulate, floating, or suspended matter cost little in comparison to the benefits.

Subtle pollutants require research

However, the next stages of cleanup require a more convincing, scientifically established reason to spend money for abatement. A kind of leapfrogging assumption of standards in these complex, subtle cases may turn out to be very wasteful.

The control of automobile exhaust is still awaiting judgment. Emission standards are now being changed from

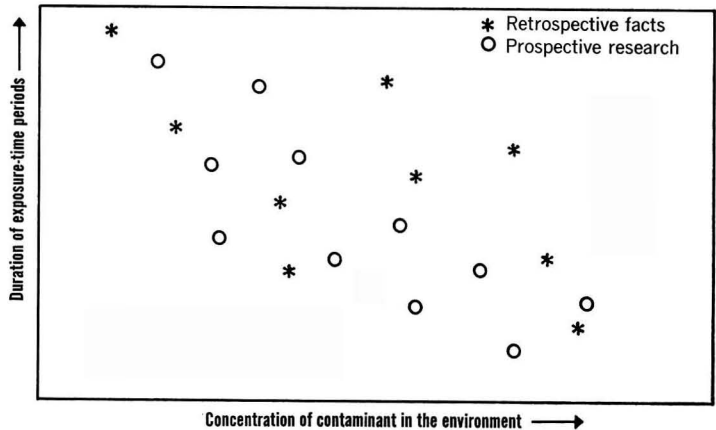
a basis of per cent of pollutant in the exhaust gas to grams per mile, a more realistic relationship. The efficiency and operating life of the control devices are in doubt. There may be an additional expense for mandatory annual inspection and maintenance. The application of Los Angeles criteria to hardware required for the entire country has been criticized. While the situation in West Coast basins requires drastic control of reactive hydrocarbons, the rest of the nation is little troubled by photochemical smog. The improved engine designs resulting from the 1968 federal regulations are possibly all that will be necessary to control hydrocarbons and carbon monoxide outside of a few California cities.

the Congress to a sequential approach in setting standards. The Air Quality Act of 1967 calls for the Secretary of the Department of Health, Education, and Welfare to issue criteria for each pollutant. The Federal Water Pollution Control Act calls for the Secretary of the Department of the Interior to establish a technical advisory committee on water quality criteria.

Criteria express the damage to health and welfare which can be expected from exposure to a contaminant at different concentrations and for different times. A criterion is simply a scientific presentation of cause and effect or dose-response relationship. Next, a judgment is made at the state level of how much damage

Environmental quality criteria—1

Examination of existing and new data on exposure of human beings, animals, plants, and materials



Criteria. Establishing criteria begins with arranging the available data for a given environmental contaminant in terms of concentration and duration of exposure. Examinations of past events are supplemented by additional research

Another area for caution is the thermal pollution of streams and estuaries by cooling water from power plants. For example, the wide adoption of a uniform temperature limit (such as 93° F.) would have enormous effects, although the limit has virtually no basis in scientific experiment. The standard would have been promulgated before the aquatic ecology research has even begun in many watersheds.

A sequential approach to standards

The recognition of the errors in cost-effectiveness judgment which can accompany a leapfrogging policy has led

society is willing to put up with, or, conversely, how much abatement the people are willing to pay for. This judgment should integrate such things as the cost of not abating, the cost of installing and operating control equipment, health effects, nuisances, and esthetic offenses.

The criterion then is used to translate the damage level into a concentration \times time value for the ambient air mass. This quantitative figure (usually expressed as parts per million averaged over a short time not to be exceeded by more than a few days per year) is an ambient air standard or a receiving water standard. Integrating

many local factors will produce different standards for different parts of the country, but some minimum acceptable quality can be insisted upon by review at the federal level.

The ambient environmental quality standard is then related to the individual sources of that pollutant. Emission restrictions can be calculated for all sources, taking into account, for example, stack height or stream flow, weather, climate, and terrain, so that the ambient quality is achieved. The economics of abatement technology may prevent reaching, for the time being, an ambient environmental quality goal. Enforcement is accomplished by identifying all sources and monitoring their emissions.

haps fortunate that there is more than enough to be done in abating gross and obvious pollution for the next few years. The big expenditures for pollution control and the massive manipulations of the environment lie ahead—in a sense it is earlier, not later, than we think. If we give careful attention to emergency situations (such as spills or persistent inversions) we have the time to do the research and construct the organizations which will guide future control of a variety of environmental contaminants.

Current legislative trends

Congress today can be said to be leading the nation toward a better environment. It originated the recent air

- Transportation, distribution, and fate of pollutants: \$20 million.

- Measurement and instrumentation: \$12 million.

- Social, economic, and legal aspects: \$5 million.

- Prevention and control technology: \$100 million.

- Effects of pollution on man, plants, animals, materials: \$45 million.

The major agencies involved include the Departments of Agriculture, Commerce, Defense, Health, Education, and Welfare, Housing and Urban Development, and Interior; the Atomic Energy Commission, National Aeronautics and Space Administration, National Science Foundation, Tennessee Valley Authority, and Veterans' Administration. It is a monumental task simply to coordinate the science and technology of pollution control.

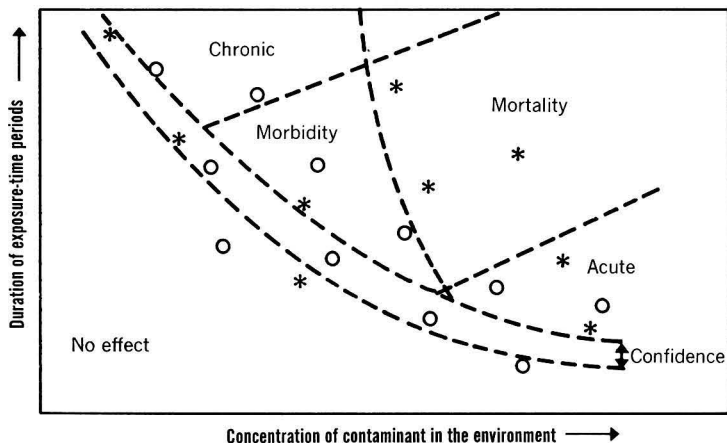
Another trend affecting legislation is that we are gaining a more sophisticated understanding of the term "quality." Cost-effectiveness is a common term in the Capitol, but it is important to pollution policy. The accepted goal today is to restore and maintain a quality of the environment without disrupting our economy and culture.

There is a great deal of uncertainty about the price people are willing to pay—in terms of money, changed habits, and restrictions on freedom of choice—for environmental quality. Of course, any proved health effects will be eliminated. And really obnoxious sights, odors, and dirtiness will be taken care of. But the quality necessary for other species and for esthetic values may seem too costly to a society which finds it difficult to understand an ecological web of life. It is not easy to quantify these benefits, but it will be all too easy to quantify the costs of achieving ever higher standards. Goals which refer to an environment with no deleterious effects on health, welfare, or the pursuit of happiness do not have much meaning in a real political context.

Laws must be legally enforceable in a practical manner. For example, odors are a nuisance, but a connoisseur of Limburger cheese might be willing to put up with an affront to the senses which others would not. More basically, an industrial valley, because of the payrolls involved, may accept a higher level of pollution than would a distant bureaucracy.

Environmental quality criteria—2

Identification of cause and effect relationships-dose and response



Effects. The exposure data are then correlated with the type of response or damage to environmental quality. A region of no effect is identified, and the confidence limits of prediction of effects are derived from the total amount of evidence. A description of the dose-response relationship is obtained

This sequence is highly dependent on the sciences which construct the criteria. Environmental epidemiology is basic to the entire process. Unfortunately, most of the evidence is empirical, and well designed research is just beginning.

Thus, legislation for environmental quality has placed an obligation on science to provide a sound, legally useful basis for the subtle pollutants which our senses cannot evaluate. It is per-

and water legislation. Where local political boundaries and industrial vested interests have prevented progress, Congress passed federal laws.

Most importantly, the government has supported research to identify pollutants, quantify their effects on health and property, and develop lower-cost, efficient means of control (ES&T, February, 1968, page 90). In fiscal 1968, it spent \$250 million in this way:

- Pesticides: \$65 million.

Opportunities and responsibilities

Chemical technology has six identifiable areas for action and response to federal policies in the environment.

First, wastes must be physically controlled. That is, the byproducts and nonusable residues from manufacturing, processing, combustion, and municipal waste disposal must be contained at all times. They must be kept apart from the living environment until they can be either recycled, permanently and safely stored, or dispersed to a satisfactory low level.

Chemical engineering processing is the key to this requirement. New plants pose less of a problem than do older ones. Waste management will be much more important to process design and to the choice among competing methods. Plant location will be less important when virtually all surface waters—streams, estuaries, and coastal areas—are brought under standards. Location will continue to be important in meeting air pollution standards because weather and terrain will affect the limitations on emissions.

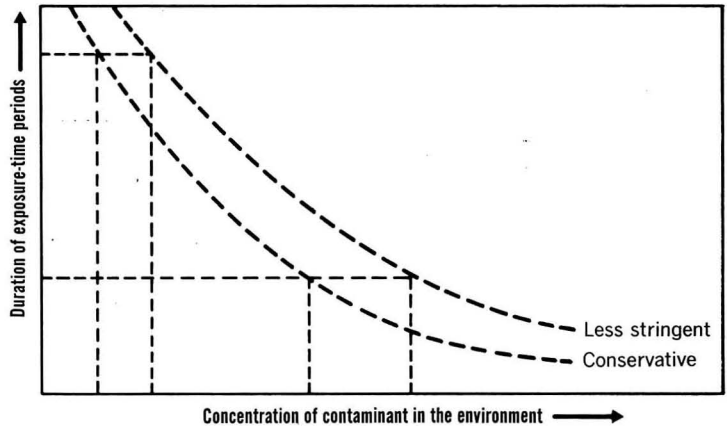
Second, materials must be recycled with greater ingenuity. This is the most direct way of lowering the costs of pollution abatement. Metal dusts, fly ash, sulfur oxides, solids in sewage plant effluent, and refinery vapors are examples of potential pollutants which can pay part or all of the cost of their containment and management if they are used in a recycle system.

Third, markets created by the pressure of pollution abatement legislation must be satisfied. For example, the annual capital investment in pollution control equipment is estimated at several billions of dollars. To monitor the environment, automatic continuous analysis of thousands of streams and hundreds of airsheds will be necessary. Chemical treating agents, coagulants, and similar materials will continue to be in demand in abatement processes. More federal R&D funds may find their way to industry if a patent policy can be negotiated that truly serves the public interest. At present, the funding agency often simply holds the rights. Licensees of federally held patents may need some exclusivity to justify spending additional money for commercial development.

Another type of market is the replacement of products which are caus-

Environmental quality criteria—3

Choose dose levels to avoid unwanted responses



Standards. Standards are chosen to avoid an unwanted degree of damage by limiting the exposure dose. Usually, a long term chronic dose is prescribed as well as a shorter term episodic exposure. Other factors such as economics, local requirements for the environment, and available technology may influence the choice of standards

ing trouble in the environment. Phosphate-free detergents, biodegradable plastic packaging, immobile nitrogen fertilizers, additive-free gasoline—these items may become competitive by virtue of the pollution created by present products. Uniform nationwide minimum standards are under study for air quality. Such standards would provide a large market base to attract private sector R&D effort.

Other markets may be disrupted. Sulfur recovered from stack gas would equal the present consumption; dislocations of conventional sulfur sources would occur, but very slowly. Another example is the nonreturnable bottle, an innovation of glass technology but the bane of solid waste control. It could be regulated out of the market if its private convenience value is exceeded by the public cost of disposal.

Fourth, the chemical industry must make a greater effort to assess the environmental effects of its products before they are introduced. A recent advisory report to the HEW Secretary recommended prohibiting after 1970 "general use of any new synthetic material, trace metal, or chemical until approved by the Department of

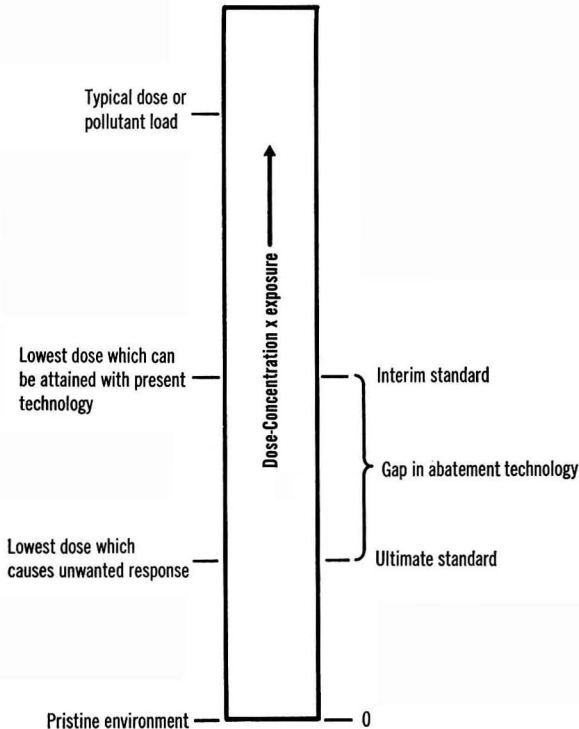
Health, Education, and Welfare." Assuming that the criteria for such approval could be established at some future date, the cost to industry of the testing involved would be enormous. Despite the utopian aspects of environmental quality via regulation, the trend toward consumer protection is plain.

Synthetic organic chemicals are foreign to the natural environment and are therefore suspect from the start. The discovery of DDT throughout the biosphere is testimony to the powerful pervasiveness of chemicals—whether or not the chemical is actually a hazard. Highly technical consumer goods give little opportunity for the buyer to beware. What product-liability laws cannot accomplish, increasing regulation will attempt.

Fifth, the chemical industry must explain its problems more frankly and in greater detail. The technical literacy of the general public is increasing rapidly. Understanding the complexities of chemical manufacture, the public may temper demands for immediate abatement or overnight replacement of offending products. The vague and elusive public relations program will not withstand the scrutiny of today's citi-

Environmental quality criteria—4

Set standards on the basis of dose-response data,
plus consideration of abatement technology,
economics, and local situations



Research and development. Treating the exposure as the product of concentration and duration, the standard may be compared with existing contamination and the pristine environment. The pristine environment will usually not be a necessary goal, and reduction of the present pollution load will usually be limited by technical-economic considerations. An interim and an ultimate standard thus become the most practical expressions of the situation. The gap between these values is an opportunity for abatement technology R&D

zen action groups, the press, and local enforcement officials.

Finally, the industry must provide more information to Congress. It is important that as many channels of science advice as possible be provided to the legislative process. Congress is far more receptive than industry believes. Rather than merely supplying defensive statements, the chemical industry can participate in determining pollution policy from the outset. Cost sharing in research, R&D patent policy,

abatement timetables, technical economics, alternatives in resource management—these issues can only be resolved in an optimum way for the nation if the industry brings its viewpoints to the discussion.

Waste management is largely a task for local governments and the private sector, but getting the job done right is everyone's business. In practical terms of profit, service, and public relations, waste management brings real opportunities to the chemical industry.



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Mr. Carpenter's contributions in the field of chemical rocket propulsion have resulted in several patents, as well as a number of publications. At the Science Policy Research Division, established to provide advice and counsel to Congress on technical matters, Mr. Carpenter has had primary responsibility for environmental pollution policy. Other issues he has studied include the transfer of technology from federal R&D programs and the social impact of applied science. He is technical consultant to the House Science, Research, and Development Subcommittee for its hearings on environmental quality. Mr. Carpenter is a member of Sigma Xi and the American Chemical Society, a Fellow of the American Institute of Aeronautics and Astronautics, and serves on the editorial advisory board of C&EN.

Incineration—A Practical and Scientific Approach

Understanding the complex process known as incineration is essential to its evolution as a basic science and as a practical and useful tool

An incinerator is a steel or refractory chamber whose purpose is to destroy domestic and industrial wastes by burning. When badly designed or operated, stack gases and other emissions from the incinerator can create public and economic nuisances in the form of smoke, grit, or noxious gases. The purpose of combustion research on incinerators is to eliminate these nuisances.

The fuel involved—domestic and industrial wastes—consists of varying proportions of three components: combustible material, noncombustibles, and moisture. Proportions of these three components vary widely depending on the sources of their constituents, but proportion of components is the basis for at least one system of classification of wastes. This system, proposed by the Incinerator Institute of America, appears in an accompanying table.

With the exception of specialized wastes of Types 4, 5, and 6, for which special incinerator systems are required, the bulk of the wastes being handled by domestic and municipal incinerators (Types 0, 1, 2, and 3), with which we are primarily concerned, consists of varying proportions of rubbish and garbage, to use these two terms as generic names.

Definitions

Rubbish and garbage have different origins. They are defined by Ziel (1965) as follows:

- Rubbish is composed of dry combustible material such as newspapers, magazines, cartons, boxes, plastic containers (and noncombustibles—metals, tin cans, glass, crockery, and dirt).
- Garbage is composed of wastes from the preparation and serving of

food (such as coffee grounds, tea leaves, vegetable leaves, and tag ends of meats, fowl, and fish). It is largely putrescible organic material with high natural moisture content. Removal from the apartment at short intervals is necessary.

These two categories provide a broad breakdown of the materials available for developing a satisfactory combustion research program on incineration. A more unpromising source of materials for a scientific investigation would be hard to imagine. At first sight, such raw material would seem to preclude the possibility of anything other than an *ad hoc* or cut-and-try testing program, and to rule out any sort of fundamental investigation.

However, *ad hoc* testing programs are notorious for their limitations. First, there is rarely any guarantee that what is found to work adequately is necessarily the best or optimum operating configuration (for example, the location and number of overfire air ports). Second, when some major factor of the system changes—for example, the proportion of garbage to rubbish in the refuse—there is no guarantee that the previously determined optimum operating conditions are still valid for the changed conditions, so the whole tedious (and expensive) testing program has to be rerun.

Therefore, we contend that the only practical and economic method of investigating combustion requirements for incinerators is some sort of fundamental program. A fundamental program, however, has its own drawbacks if not properly formulated and controlled, since fundamental research, if it gets out of hand, can prove to be even more expensive than cut-and-try testing and, as an end product, does

not provide even an inadequate practical working system. The essential problem is that the possibilities for doing experiments are just too large. Many experiments performed under such conditions are trivial, or irrelevant, or too limited, or too costly for the information yield. And without adequate analysis, thought, and selection, the proportion of significantly useful experiments is often too low. This is a point of view forcefully expressed quite recently by Platt (1964) who argued that much more careful thought should be given to the possible outcomes of any experiments undertaken, particularly if they are very costly. As an example, he cites the increasing use in high energy physics of groups of experimenters to debate the potentialities of different experiments beforehand and to select the best experiment on the basis of precision of formulation and yield of information. This is particularly important in high energy physics because of the cost of each experiment. It is quite easy to do an adequate or even a good experiment, but an adequate experiment is still a waste of time and money if it is not the best experiment.

In incinerator research we have precisely this problem. The need for information is urgent. The cost of research is high. The basic information already available is meager. The possibility and ease of performing experiments of low-information yield is too great. A method of selecting the best experiments in a carefully formulated program is required. This, according to Platt, should be an integral part of the research and rate as highly as the performance of the research itself.

Such a formulation in an area such as incineration may be unusual, but in

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our view, is possible and necessary. The method of selection is primarily based on elimination of the irrelevant, the trivial, and the less necessary, as this approach generally leads to fewer errors than intuitive guesses as to the best experiments.

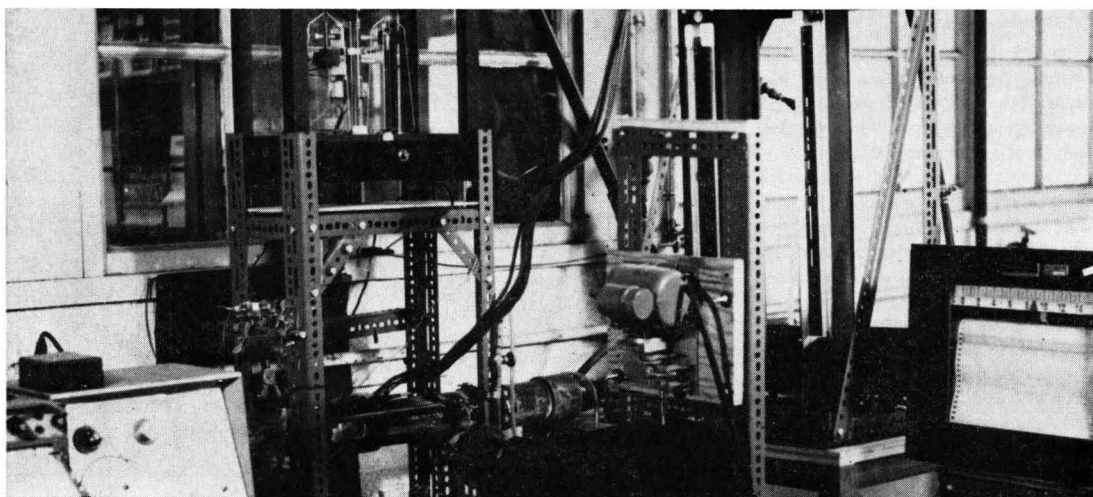
The purpose of this paper is to present such a formulation, together with the reasoning behind it (sometimes referred to nowadays, somewhat pretentiously, as the philosophy of the research). In addition, we will give a brief summary of the progress of the work so far undertaken in our research program, sponsored by the Public Health Service.

Analysis and approach

In analyzing the overall problem of incinerator requirements, and breaking it down into components for the purposes of research, we are today in the advantageous position of being able to draw on the experience of the International Flame Research Foundation (IFRF). This group has been in operation for about 20 years, with experimental furnaces in Holland. Apart from the nominally more varied types of fuel with which we are faced in incineration, the problems involved are very similar.

So far as the IFRF was concerned

at its inception, the state of the combustion art in industry owed more to "know how" than to "know why," so that any combustion problems developing, of which there were many, had to be solved largely by trial and error. This approach was tedious, time-consuming, and expensive. However, although the development of the necessary "know why" was beyond the capacity of many of the organizations concerned, many of the combustion problems were common at a more fundamental level to the varied industries and situations in which they arose. The IFRF, therefore, undertook to investigate flames that were of a realis-



Paper spheres. General view of equipment for study of suspended paper spheres combustion (Program A, M. Kuwata). The spheres are suspended from the balance in the horizontal tube (below) in which air or oxygen-enriched air flows from right to left. The balance has a continuous weight-sensing attachment with continuous read-out on the recorder (left). Air and oxygen flow is monitored by rota-

mers (right rear). The multipoint 24 temperature recorder (extreme right) is used for recording temperatures at six points inside the burning spheres. A camera (central foreground), largely covered by a black cloth, is used to record size changes to match with the weight changes to determine density changes from pyrolysis or internal burning. This equipment is used for fundamental kinetic data

tic engineering size (in furnaces of cross section 5 feet and length 30 feet) but yet were grossly simplified or idealized from the point of view of ultimate practical application.

Several reasons were advanced for the restrictions (from the ultimate application point of view) on the size and complexity of the flames examined. First, the investigations were so fundamental to the applications engineer that individual organizations could base development programs on this fundamental work, with more than sufficient latitude to develop different competitive combustion systems for marketing. Second, for the IFRF, to undertake all the varied development work required by the supporting organizations would be prohibitively expensive to the foundation. Finally, the simplified (or fundamental, or idealized) flames were soon found to be extremely complex—so complex that not only has it taken 20 years to develop some broad level of understanding of these simple flames, but it has also required the support of a wide range of individual research projects on various aspects of different parts of the problem carried out in a number of government, industrial, and university research laboratories in several countries.

Programmed research

As a participant and director of one of these “fall out” programs, we had occasion to analyze the requirements for programmed research into the fundamentals underlying the behavior of the simple engineering flame. Our analysis resulted in a concept of successive development of complexity of the pulverized coal flame, a concept that was later successfully applied to the incinerator problem (Figure 1).

This diagram shows three broad levels of research. At the lowest, or most fundamental level, are the four basic sciences involved in all combustion systems—reaction kinetics, materials properties, heat transfer, and aerodynamics. The diagram then shows a progressive buildup of complexity—and therefore of understanding, as the necessary research is completed—as the results of the basic sciences are incorporated one by one into the research scheme. This may reasonably be called the technological level of research. Finally, at the level marked

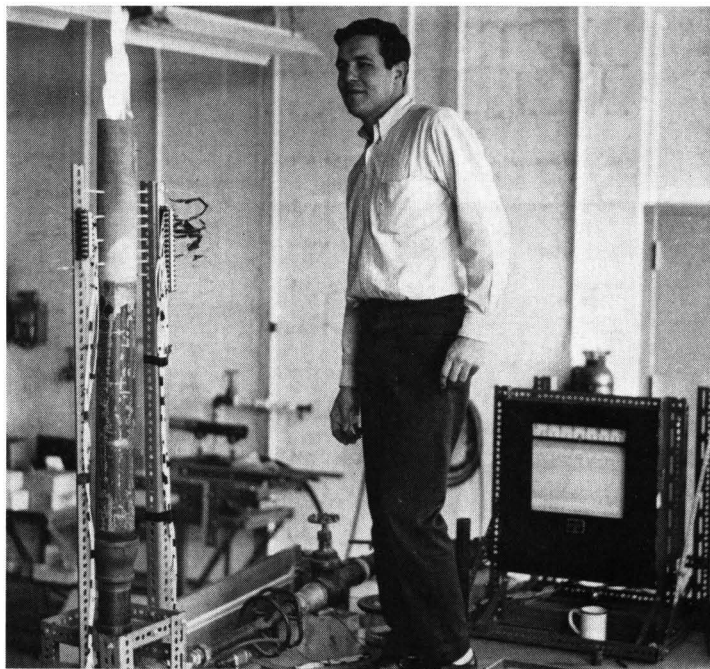
“Test incinerator” and above, we have the level of development engineering. As the figure also illustrates, each broad level is broken down into a number of intermediate steps emphasizing that applied research ranges from the fundamental sciences as a continuum through technology to engineering development and finally to application.

With Figure 1 as a background, we can say something about the advantages and disadvantages of different approaches to the problem of research planning. We can identify the top two steps, Pilot plant and Industrial plant operation, as the levels of *ad hoc* or cut-and-try testing, if this is carried out in isolation and without the more fundamental supporting programs. This sort of operation can lead only to “know how,” since the complexity of the system will rarely allow an appreciable level of understanding beyond intuitive guesswork.

Empiricism

In the context of getting practical systems to work quickly, so that one has something to analyze, empiricism and the development of “know how” has quite a lot to recommend it, since this frequently acts as the cutting edge that carves out the fundamental problems. An excellent example is the discovery of the principle of hydrostatics by Archimedes in the process of solving the practical problem of adulteration of a gold crown. However, beyond a certain state—which incinerator technology reached some time ago—further empiricism becomes a waste of time. More fundamental work is required, and it is in this sense that we have interpreted the call by the Building Research Advisory Board for research to improve the combustion process. The board singles out for more detailed investigation:

- Design, geometry, and size of combustion chambers.



Simulated fuel. Equipment for study of a simulated fuel bed by newspaper rolls or wooden dowels packed in a combustion pot (Program B, J. P. Stumbar). Newspaper rolls or dowels are packed in the top of a 3"-diameter vertical steel pipe. Air, which is supplied from below, is metered by a calibrated asymmetric venturi (bottom left). The packed bed is ignited at the top. Thermocouples for temperature measurement are inserted through holes drilled in the steel pipe, with read-out on a multipoint temperature recorder. This equipment has been used to determine that the flame spreading downward is accelerating

- Amount, location, and effect of combustion air.

- The location and distribution of auxiliary heat.

- The influence of ventilation.

These are the factors to be included in any more fundamental program.

If more fundamental research is required, the next problem is to decide at what level of fundamental it is to be carried out, because fundamental is a very relative term (see Figure 1). If we wish to engage in the polemics of semantics, we could draw an arguable distinction between fundamental and basic, and assign the word basic to that level of research which is generally regarded as being the most fundamental and where the implications of application are generally least obvious. The purpose here, however, is to make a real distinction between several levels of supporting research—basic, technological, developmental, and the like

—that are fundamental to the pilot and industrial plant, but that can be ranked in an order of being more or less fundamental to each other. The background problem, as remarked earlier, is that fundamental problems are equally capable of getting out of hand if they are not correctly chosen and carefully planned.

In general, we find that the more fundamental the investigation, the greater the generality of the results and the wider their application, but more development work is then required before the results can be put to use, and vice versa. To put the problem another way, we still have too many choices, and these have to be narrowed. This can be done in several ways.

Narrowing the choices

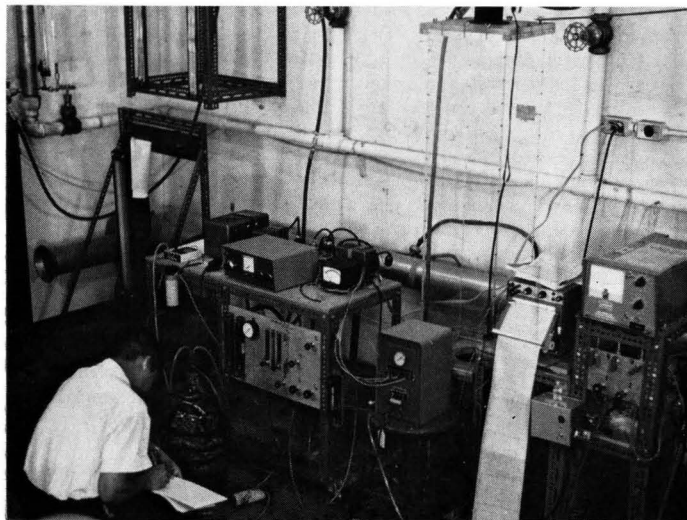
We have already ruled out the desirability of working at too applied a level, but we can take this one stage

further and exclude all levels of (development engineering) research above the test or idealized incinerator. This approach satisfies a number of conditions. First, each step in the progression in Figure 1 generally represents an increase of an order of magnitude in the physical size of the equipment, the cost of the operation, and the time taken to complete it. Development engineering programs, therefore, are generally too costly in terms of money, manpower, space, and time for any university-oriented program. Second, such projects are better suited to operation by research institutes or to in-house research by any competent interested company, thereby not jeopardizing the competitive positions of the participating companies. Certainly, the Federal Government should not finance research that would impair competition. Finally, elimination of the larger-scale, applied aspects of the research satisfies university educational requirements. Any units of the programs that are formulated shall then be mainly operable by a single student and would satisfy the academic objectives of originality and other requirements for a higher degree.

The test or idealized incinerator, therefore, represents an upper bound. We may now consider requirements of a lower bound. Here we have a simpler task altogether. We will assume the existence of an adequate level of knowledge and understanding of the four basic topics specified. Our problem will be the permutation and application of that knowledge to the incinerator or its subcomponents as indicated in Figure 1. In practice, experience has shown that there are generally a few gaps to be found at the basic level and that still more fundamental programs may have to be formulated in due course, but that can be ignored for the time being.

We have, therefore, isolated the Technological level of the Figure 1 breakdown as the level at which research should be undertaken. A further question is whether all stages at this level should be attacked. The answer we give from experience is that this is generally desirable and sometimes necessary. As a minimum research operation, we have planned, and are currently implementing, four programs:

- Investigation of the kinetics of typical waste materials during reaction.



Mixing. General view of equipment for the study of mixing behavior using isothermal air models (Program C, T. R. S. Rao). The program started with a general study of overall mixing requirements for Bragg's mixing criterion—a stirred reactor section followed by plug flow—to be satisfied. Mixing occurs in the rectangular Plexiglas box with air and tracer (either carbon dioxide or helium) supplied through a swirl attachment at the top of the box. The sampling point is the box exit. Carbon dioxide is analyzed using the LIRA (right); helium is analyzed by GOMAC units (center and left). The method of experiment is to establish a steady state concentration of tracer in the mixing chamber, and then to stop the tracer (by closing an electromagnetic valve). The resulting decay of concentration monitored at the outlet has a characteristic form for different specific gross mixing patterns inside the mixing chamber. The objective of the experiment is to determine what method of supply in introducing the fluids will give the closest approximation to Bragg's ideal pattern

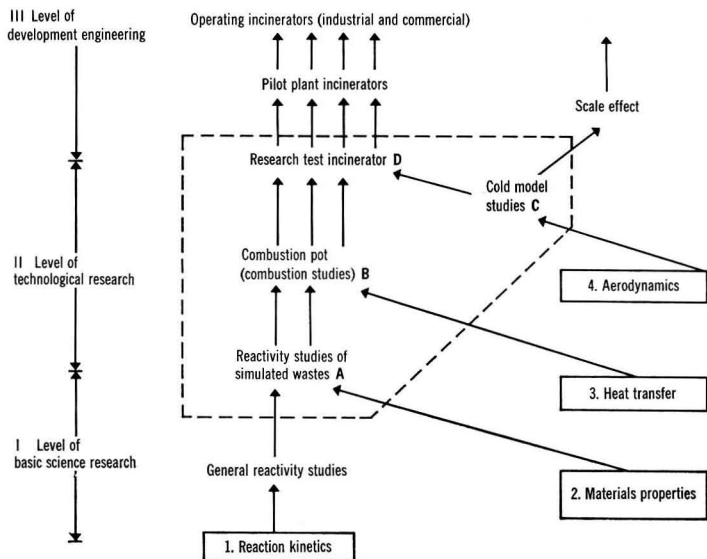


Figure 1. Schematic breakdown of overall research requirements into successive stages, indicating: • The three general levels of basic, technological, and development research. • The relationship between the three levels. • The area selected for investigation in the subject program (inside dotted line). Letters specify the four different programs described

• Combustion study of burning bed behavior in a small combustion pot.

• Cold model studies of the aerodynamic patterns in an incinerator, particularly with respect to mixing.

• Construction and instrumentation of a small test incinerator.

Subject selection

Although the preceding arguments might lead one to the conclusion that an appropriate program should be broken into several stages or constituent investigations at the technological level, this generalization has to be given more precision if any useful action is to be forthcoming. Planning and implementing some programs of investigation at several different sub-levels is not enough. In accordance with Platt's propositions, they have to be the right programs that will appropriately integrate with each other in due course to build a complete picture. The technological area has to be broken down into a set of topics in some logical way, and an appropriate selection from that set has to be made. As an initial aid to this breakdown, we will take a fresh look at the practical problem again, but from a different point of view.

The practical problem involved in incinerator behavior is elimination of the emission of smoke, grit, and noxious gases. In discussing the problems of incinerator behavior, we frequently

hear it said, in a colloquial sort of way, that one objective is to stop them from producing smoke. This is always meant in the sense of emitting smoke, but there is an important distinction between production and emission. To make this explicit, we can say that so far as behavior inside the incinerator is concerned the production of smoke is irrelevant, just so long as no smoke, grit, or noxious gas ever crosses the real or imaginary boundary between the incinerator and the outside. In other words, the practical problem is also a boundary condition, at least metaphorically.

Practical problems are commonly found to be boundary conditions to some more fundamental problem, in the real as well as the metaphorical sense, and the incinerator is no exception. We have here the situation that if we regard the incinerator as being essentially a problem in combustion, then solution of that problem is possible only if we have complete information on the boundary conditions. To put it another way, suppose we have complete information on the equations, constants, input data, and similar factors governing behavior of an incinerator. Then we are not only able to predict the precise behavior inside the incinerator, but we must also be able to predict with equal accuracy the amount of smoke, grit, and other emissions crossing its boundary. And we can

compute the input or other conditions that will eliminate the smoke and grit crossing that boundary. In other words, since the practical problem is literally a boundary condition to the fundamental problem of combustion behavior, complete solution of the fundamental problem will provide, as a by-product, a complete solution to the practical problem.

This phenomenon, in fact, turns the whole problem inside out—a common characteristic of practical problems. Indeed, it is so characteristic that a useful short cut in analysis is to concentrate on searching for the fundamental problem to which the practical problem is a boundary condition.

By the above argument, we have reached substantially the same conclusion as we did earlier in this paper, but by a different route. Indirectly, we have also obtained a statement of our research objective in somewhat more precise terms, our objective being to obtain information on the equations, values of constants, and other factors governing combustion behavior in the incinerator. The next problem is to determine what programs are necessary to achieve these objectives.

Problem breakdown

Since we need information on the governing equations, we can circumscribe the problem still further by using the concepts of dominance and control. These concepts hold that we need concern ourselves only with parameters of some relevant or significant magnitude, where the criteria of relevance or significance have to be determined for each individual parameter. Conduction and convection, for example, are often ignored in favor of radiation so far as heat transfer to the surface of the fresh fuel inside the incinerator is concerned. Also, the inherent kinetics of the reacting system

are frequently (and perhaps erroneously) neglected in favor of a diffusional dominance of the burning rate. In the same way, we can inspect possible extremes of behavior in the incinerator, and reduce the number of situations that we need to analyze, by elimination of those that are obviously secondary.

To do this, we first have to identify the possible modes of behavior of an incinerator. This can be done in several ways, but our choice is to regard the incinerator as a box divided essentially into two zones. Zone I is that of the solid fuel bed through which underfire air is passing and that, ideally, is burning steadily. Zone II is the overbed combustion volume in which gaseous combustibles (including smoke) are mixing with overfire, air, and, perhaps, are burning.

We now recognize several possible modes of behavior of the reacting materials, of which smoldering and flaming combustion represent two extremes. These two modes can be defined with greater precision by also recognizing that they represent unignited (smoldering) and ignited (flaming) conditions, where ignition is defined formally by satisfaction of the Van't Hoff-Semenov criterion. According to the thermal theory of ignition as discussed extensively by Semenov (1935), Frank-

Kamenetskii (1955), and Vulis (1961), ignition occurs in a system when:

- The rate of heat generation by reaction equals the heat loss.

- The differentials with respect to temperature of the heat generation and loss are also equal. There is then (theoretically) an almost discontinuous jump in temperature—the Semenov jump—that characterizes ignition.

In this type of thermal analysis, however, reaction of the material below the ignition temperature is never ruled out (although it may in some cases be trivial). We may, therefore, distinguish between *reaction* when there is continued interaction between the reactants below the ignition temperature, and *combustion* above the ignition temperature.

Since this condition of reaction and combustion applies both to the fuel bed (Zone I) and to the gas phase above it (Zone II), we obviously have four possible modes of reaction that are differentiated quite precisely by whether the zone temperatures are above or below ignition. These possibilities have been set out in Table I. Smoldering and flaming combustion represent the extremes, the first being the situation of no ignition in either zone, and the second corresponding to ignition in both zones.

Since this breakdown of Table I

gives us four possible reaction modes, our question must now be whether we need to investigate all four. The answer to this, which we obtain by systematic elimination, is that we shall be really interested only in Mode 4, flaming combustion.

The criterion we use for this selection is that of practicality. The purpose of an incinerator, after all, is disposal of wastes. In principle, any of the four modes is capable of achieving this objective, but Modes 1, 2, and 3 can be eliminated by the test of practicality. Let us consider first Mode 1, smoldering. We can eliminate smoldering as being unimportant to us (at least initially) on the grounds of smoke production, equipment size, or small throughput. Smoke can, of course, be eliminated by the use of afterburners of one form or another, but this is undesirable (if it can be avoided) because of the cost of the auxiliary equipment. This same objection simultaneously eliminates Modes 2 and 3.

The second argument, which also eliminates Mode 3, is the matter of equipment size or small throughput. If the solid bed is unignited and only smoldering, then the time taken to burn up the waste is far too long unless the equipment is unnecessarily large and costly.

Clearly, the only reaction mode that we should consider as being practical is that of flaming combustion, with a state of ignition maintained in both zones. This decision gives us a further breakdown of topics to be considered. First, if flaming combustion is to be initiated, we must be able to answer question 1A: What are the conditions for ignition?

Second, if flaming combustion is to be maintained, we have to be sure that the combustion reaction is not extinguished in either zone, so we have to be able to answer question 1A's counterpart, question 1B: What are the conditions for extinction?

If we can answer these two questions and guarantee meeting their requirements, flaming combustion will be maintained. But these are merely minimum or necessary conditions. There is still no guarantee of efficiency of burn-up (particularly of smoke). Therefore, we have to have some information on reaction mechanisms so that these mechanisms can be opti-

TABLE 1 Possible reaction modes in an incinerator

Mode	Reaction type	Condition of:		Consequences
		Zone I: solid bed	Zone II: gas phase	
[1]	Smoldering	Reaction only: unignited ($T < T_{iR}$)	Reaction only (negligible): unignited ($T < T_{iR}$)	Long reaction time. Produces smoke
[2]	Combustion	Combustion: ignited ($T > T_{iR}$)	As above (Mode 1)	Reaction time reduced Produces much smoke
[3]	Burning	As in Mode 1	Combustion: ignited ($T > T_{iR}$)	Smoke and other volatiles burning: normally only with ignition torch
[4]	Flaming Combustion	As in Mode 2	As above (Mode 2)	Burning of smoke: usually self- sustained with partial to complete burn-up of smoke

TABLE 2 Classification of wastes to be incinerated

Classification of wastes Type Description	Principal components	Approximate composition (% by weight)	Moisture content (%)	Incombustible solids (%)	B.T.U. Value/lb. of refuse as fired	B.T.U. of aux. fuel per lb. of waste ^c	Recommended min. B.T.U./hr. burner input per lb. waste
^a 0 Trash	Highly combustible waste, paper, wood, cardboard cartons, and up to 10% treated papers, plastic or rubber scraps; commercial and industrial sources	Trash 100%	10%	5%	8500	0	0
^a 1 Rubbish	Combustible waste, paper, cartons, rags, wood scraps, combustible floor sweepings; domestic, commercial, and industrial sources	Rubber 80% Garbage 20%	25%	10%	6500	0	0
^a 2 Refuse	Rubbish and garbage; residential sources	Rubbish 50% Garbage 50%	50%	7%	4300	0	1500
^a 3 Garbage	Animal and vegetable wastes, restaurants, hotels, markets; institutional, commercial, and club sources	Garbage 65% Rubbish 35%	70%	5%	2500	1500	3000
4 Animal solids and organics	Carcasses, organs, solid organic wastes; hospital, laboratory, abattoirs, animal pounds, and similar sources	Animal and human tissue 100%	85%	5%	1000	3000	8000 (5000 primary) (3000 secondary)
5 Gaseous, liquid or semi-liquid	Industrial process wastes	Variable	Dependent on major components	Variable ^b	Variable ^b	Variable ^b	Variable ^b
6 Semi-solid and solid	Combustibles requiring hearth, retort, or grate equipment	Variable	Dependent on major components	Variable ^b	Variable ^b	Variable ^b	Variable ^b

^a The above figures on moisture content, ash, and B.T.U. as fired have been determined by analysis of many samples. They are recommended for use in computing heat release, burning rate, velocity, and other details of incinerator designs. Any design based on these calculations can accommodate minor variations. ^b According to wastes survey. ^c Data to be included in combustion calculations.

mized, so there are two other paired questions to be considered, question 2A: What are the reaction mechanisms? and question 2B: What are the optimum reaction conditions for most complete burn-up? This last question represents a sufficient condition.

Once again we can say that these four questions must be applied to both zones in the combustion chamber, but they apply with some different emphasis in the two zones. Therefore, we can again apply some priority and selection in the evolution of the program.

In Zone I, initial ignition always requires some sort of ignition burner or other initiator. Once combustion has started, the initiator is commonly turned off, and all we have to be concerned with then is extinction. The priority question is, therefore, question 1B. Knowledge of the mechanisms of initial ignition by an igniter would be helpful and interesting, but at present this must be relegated to second place as a question for the future. However, flame spread will probably be closely related to extinction. Next, answering question 1B requires information about reaction mechanisms which is also required for question 2B, so there is some overlap between the questions. However, we have again the

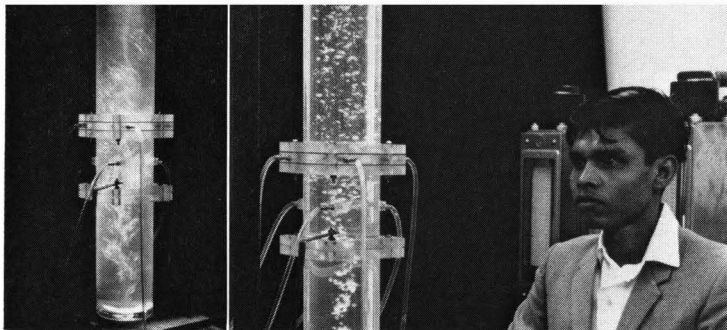
situation that question 2B can initially take second place to question 2A, since in Zone I we are concerned only that the solid bed will burn away reasonably fast and stably with production of gaseous combustibles, and optimization of conditions depends much more on Zone II.

In Zone II, ignition of the combustible gases is much more critical. The system is also much more sensitive to extinction of the overbed flame, so questions 1A and 1B have about equal priority. Fortunately, however, the ignition and extinction conditions are more closely related in this zone when the critical ignition source has been turned off than is the case in Zone I, so these two problems can, in principle, be solved simultaneously. In this zone, question 2B concerning optimization is also crucial, but we are in the fortunate position of having already studied optimized conditions for ignition, extinction, and burnout in 1967 for the Department of the Navy, and having reduced the number of situations and questions quite substantially. For research purposes, we can separate the two zones and, initially, investigate them independently before we make our selection of crucial topics.

We now have sufficient information

to be able to select the crucial topics and to construct appropriate programs for their investigation. We already know that we require at least one program for investigating Zone I behavior and one for Zone II. We shall have to combine these at some stage, so we shall also require another program to study the overall behavior in a test incinerator. However, there is still some further selection to be made. Before considering these aspects, there is one further useful simplification that can be made with respect to the nature of the materials used.

One of the potentially most complex problems in incinerator research is that of the nominally varied nature of the waste materials involved. On closer inspection, however, this is much less of a difficulty than was anticipated. Although a broad division of the materials into rubbish and garbage seems to indicate at least two different sources as an absolute minimum, nevertheless, the combustible components in both groups are carbohydrates, the prime difference between them, from our point of view, being the quantity of moisture they contain. On a B.t.u. value, it is clear that waste Types 0 to 3 are identical, being based on a heating value of 10,000 B.t.u./lb. of



Patterns. Flow patterns in supplementary isothermal (water) models Program D, B. K. Biswas) to determine by qualitative observation an optimum location of secondary air jets generating counter-vortex flow above a solid fuel bed. Intuitive and other considerations indicate that the counter-vortex flow should be at least an adequate—and possibly an excellent—configuration. Counter-vortex flow should be satisfactory for initial experiments on the test incinerator. The results coupled with those from Program C should establish whether the counter-vortex configuration is, indeed, the best. The equipment here includes a Plexiglas model with water flow vertically upward, carrying air bubbles as tracers with secondary fluid injected through eight nozzles in two sets at two levels. Each set generates a vortex in the opposite senses to each other

dry, inert free (DIF) solid, which is then corrected for the inert fraction (5–10%) and the moisture content (10–70%). This means that measurement of the moisture content should give a calorific value to approximately 10% accuracy.

What we are really dealing with, therefore, is primarily carbonaceous materials of roughly similar constitution, varying principally in the moisture content. With even greater precision, we can identify the nature of the material as being primarily cellulosic in origin. As a first approximation, we can restrict our investigations to paper and wood of varying degrees of wetness or extraneous moisture. Our experience with coal combustion suggests that this approximation should hold generally to within $\pm 20\%$.

The chief discrepancy to be expected, if any, between the burning behavior of the garbage and wetted rubbish will probably lie in the different behavior of inherent and extraneous moisture. This potential source of difference will be ignored at first since this approach will be justified by results if the nature of the moisture turns out to be unimportant. If the nature (inherent or extraneous) of the moisture is important, it will be identified by discrepancy in behavior, and a decision can then be made about means of dealing with it.

Zone I

The requirement for Zone I is pri-

marily to determine the extinction conditions, and secondarily to determine something about burning rates with a view to optimizing them. We know from analyses of thermal explosion theory that extinction depends on a balance between heat production by reaction and heat losses. Of these two factors, existing knowledge of heat transfer far outweighs knowledge of the reaction mechanisms and the constants involved.

Two programs have been initiated in this area, one for a study of the reactivity of the cellulosic material by itself (Program A), and another for study of burning and extinction in a small combustion pot (Program B).

Zone II

In the gas zone we have a somewhat different problem, centering initially around the question of flame stabilization. We can state the problem in the following terms. The fuel bed can be regarded as a smoke generator, and, in a vertical chamber such as a single flue incinerator, the smoke and other combustible gases will rise essentially in plug flow up the flue. In other shaped chambers, an axis can generally be defined with respect to which there is still substantially a nonrecirculating flow in many cases.

This smoke column is one in which we have to create a stable flame zone by some means, and then generate the optimum conditions for fastest burn-out. The conditions for this are now

known, from previous analyses of combustion chamber design, to need a well-stirred section right above the fuel bed, followed by a reversion to plug flow. The stirred section, if correctly generated, acts both as the igniter and the flame holder. The crucial element of this part of the system is the mixing behavior. To study this behavior, cold model experiments have been planned (Program C).

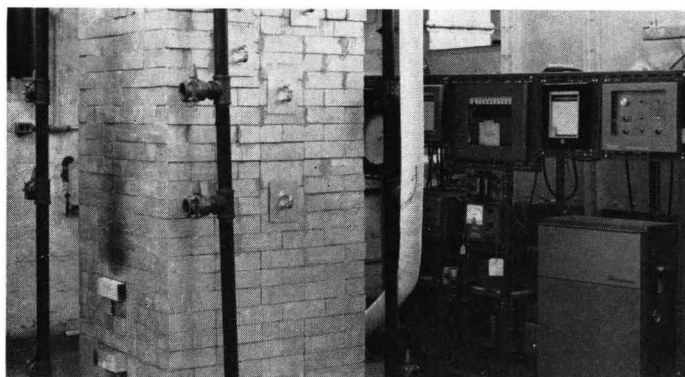
One of the objectives of the cold model experiments is to determine the optimum mixing pattern for the overfire air that will generate the crucial stirred section that reverts to plug flow. The concepts developed will then be tested in the test incinerator, which is otherwise planned to act as the focus and integrator of the more fundamental experiments.

The situation is that, although some degree of separation of the zones for research purposes is possible, in a real system there is coupling of behavior between the zones, notably as the result of thermal feedback from the overbed flame. The extent of this coupling is one of the reasons for a real distinction in bed behavior between Mode 3 (burning) and Mode 4 (flaming combustion). The test incinerator therefore comprises Program D.

Some useful progress has been made in the analysis, planning, and execution of the research programs to be undertaken, and we will summarize it briefly. Of the four programs planned, one has now been in progress for 2½ years (at the time of writing), two for 18 months, and, for the fourth, the test incinerator is being prepared as a facility for this program to start operating in a few months' time with some preliminary experiments using water models currently in progress. Since two of the programs have required the creation of facilities of some magnitude, the progress in terms of results and conclusions is still somewhat meager. Nevertheless, progress of some significance can now be reported.

Program A

This program, a reactivity study being undertaken by M. Kuwata, is currently the most advanced. A method has been devised of making paper spheres out of a pulp formed by rapid mixing of shredded paper and water. The spheres, of different diameter, are dried and then burned in air or an oxy-



Test incinerator. The test incinerator is a simple box. Instrumentation, which, as shown here, is partially complete, includes monitor gas analysis in the stack exit located behind the incinerator (for CO_2 , CO , and O_2), and quantitative smoke and grit (CEGRIT) samplers. Also, ports can be opened in the side wall by removing the bricks attached to the handles for water-cooled probe insertions for mapping the flame patterns in the incinerator. The instrument rack for the analyzers is already installed (background). The vertical black pipes are for secondary air supply. The outlets are to be connected to secondary-air over-fire parts when the most probable optimum position has been determined by the water model studies

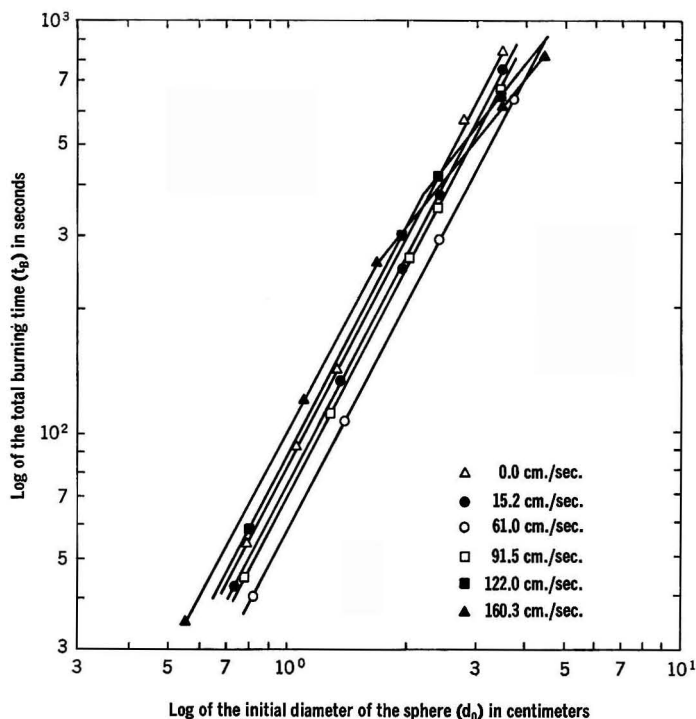


Figure 2. Dependence of the log of the total burning time (t_b) on the log of the initial diameter (d_0) of the sphere at a series of constant air flow velocities (Program A)

gen-enriched air stream at different flow velocities. The spheres are suspended during this operation from a continuously-recording balance, and burning time is determined under different conditions of sphere diameter, ambient velocity, and oxygen concentration.

The results obtained are already too numerous to present in detail but, briefly, they have been used to test existing theory of particle and sphere combustion, and the results show substantial agreement with prediction. The principal result is that, in spite of pyrolysis in parallel with the solid combustion, the data largely obey the well known Nusselt "square-law" equation between burning time, t_b , and initial diameter, d_0 . This has the form $t_b = Kd_0^2$ where K is a burning constant whose value changes with velocity and oxygen concentration. Figure 2 shows a set of some of the data plotted in agreement with this equation.

The principal conclusion to be drawn from these results is that the rate of the reaction is dominated (as expected) by diffusion. However, above a certain flow velocity and diameter, the line breaks discontinuously as shown in Figure 2, with the diameter index dropping from 2 to 1. The interpretation of this, though still tentative, is in agreement with theory predicting a discontinuous transition from diffusion to kinetic dominance. If this interpretation can be confirmed, the break point will enable us to predict velocity and other conditions under which the boundary layer is thin enough to allow a kinetic dominance of the reaction and in which diffusion can be neglected.

Program B

Although Program B, on the combustion pot, is less advanced, a satisfactory experimental method now seems to have been devised by J. P. Stumbar in which a substantially planar reaction zone is formed at the top of a fuel bed in a cylindrical pot, and this moves upstream against the air flow. Initially a refractory pot, loaded with some of the smaller paper spheres with air flowing up, was used. When the spheres were ignited at the top, flame was able to spread down against the air flow quite rapidly, most probably by a radiative process, since ignition centers were observed to form at

crevices created by the juxtaposition of two or more spheres.

There were, however, difficulties in manufacturing spheres in sufficient quantities for many experiments, so alternatives were tried. One was a roll of newspaper otherwise blocking a 3" diameter steel tube. Sufficient air could be forced through the roll to allow intense combustion at the downstream end. This is a system that holds promise for further investigation in due course, but it has been temporarily abandoned for other materials, mainly because of nonuniform combustion. If the roll is not wound evenly, more air will pass through the roll at one point than at another, and combustion at the cross section is not even. Nevertheless, further examination of this system may yield information on how to deal with stacked newspapers, magazines, and books, a difficult problem present in most incinerators.

The newspaper rolls were then replaced by wooden dowels. With more regular packing, the whole bed burns down more uniformly. Thermocouples can be inserted into the bed so that temperature profiles (Figure 3) can be obtained at several different planes. The rate of flame travel can also be determined, typically 0.1 to 0.3 inch per minute, and generally rising as it burns down.

Flame spread against an air flow is then quite feasible. However, it should extinguish either at a low or a high velocity. In that event, there should be an optimum rate of spread, and determination of this, together with extinction velocities, will be one of the additional objectives of this program.

Currently, the combustion pot experiments have been suspended for a more intensive examination of flame spread, but they will be resumed when

the auxiliary experiments have been completed.

Program C

The objective here, as stated earlier, is to determine the best method of injecting overfire air in such a way that the bottom of the smoke column above the bed is broken up into a stirred region. This objective is illustrated in a general form in Figure 4.

The incinerator is a special example of a more general problem, that of mixing. The cold model studies are therefore being set up primarily to study mixing patterns in general, with the expectation that the incinerator problem will be solved as a byproduct—another example of a practical problem being a boundary or special condition of a more general, fundamental problem.

Since the objective is to determine the division of the total volume into a stirred section and a plug-flow section, the method of experiment, similar to that used by others, follows the rate at which a gas tracer (CO_2 or He) clears from an air stream. The existence and size of a plug flow section appears as a continuation of the full tracer concentration even after the tracer input has been cut off. A stirred section shows up as an exponential concentration decay with a characteristic time constant.

Initial experiments have now been carried out by T. S. R. Rao, using CO_2 tracer in air injected through a concentric jet burner into a 4 ft. x 1 ft. x 1 ft. Plexiglas model. The mixture is monitored at the exit and analyzed continuously, with pen-recorder readout, by an IR analyzer. The initial experiments have been carried out with and without swirl. Further experiments are also planned using water models.

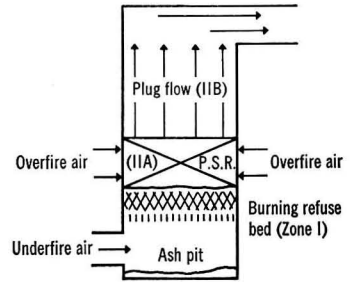


Figure 4. Proposal for incinerator study for smoke burnup above refuse bed (Zone I). Objective of overfire air is to break up plug flow of smoke and combustion products and create a P.S.R. flame-holder section for smoke ignition (Zone IIA), and plug flow for burnout (Zone IIB) (Program D)

The experiments indicate that the method should be adequate to determine the optimum arrangement for the overfire air to be used in the test incinerator.

Program D

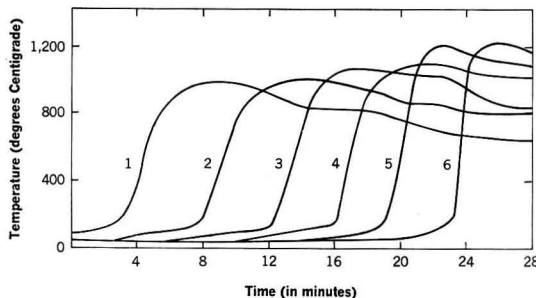
For the final program, a test incinerator has been built of superduty firebrick. This is a box of square cross section, 2 ft. x 2 ft. internally, with 9-inch walls. Apertures exist at various points for insertion of probes, and a perforated steel plate sitting 9 inches above the bottom of the ash box is used as a grate. The overall height is about 10 feet, with a side flue at the top of the stack. Air is to be supplied as underfire and overfire air from separate sources.

Instrumentation is not yet complete, but it includes an optical (light beam) smoke meter in the stack and a monitor gas sampling probe (also in the stack) for monitor gas analysis. The gases to be analyzed include CO , CO_2 , O_2 , and moisture, using several different instruments and analyzers.

Yet to be incorporated are wall and roof thermocouples and the overfire air ports. The latter will be inserted when some initial water model tests devised by B. K. Biswas are complete.

Since problems of space and logistics will prevent the continued operation of the unit over a period of hours, it will be operated essentially on a transient state basis, which also repre-

Figure 3. Temperature/time curves at selected heights within the burning bed. Positions are one inch apart (Program B)



sents a particularly stringent set of operating conditions. If problems of smoke and grit emission can be solved for these conditions, there should be no problem in the case of continuous, steady operation.

Incineration is such a complex process that direct investigation of operating incinerators can usefully develop only more "know how" of operation, but is unlikely to lead to better understanding or "know why." Although this approach could possibly lead to more immediate improvements of a limited number of incinerator types in a limited range of operations, such improvement is not guaranteed, and any improvements would be of limited range and flexibility.

There is likewise no guarantee of improvement as the result of more fundamental research, but comparative experience (such as that of the IFRF) suggests that understanding of the processes is a prerequisite to improvements beyond a certain stage of development, and this understanding requires fundamental research.

The possibilities for research operations, however, are so wide that some listing and selection of priorities is necessary to avoid waste of time and money. Such analysis is as significant and crucial in solving the problems concerned as the actual research.

The analysis presented leads to the elimination of research projects at both the engineering development level and the basic sciences level in favor of research at the intermediate technological level, at least as an initial step. For understanding behavior of even a test incinerator, continued analysis led to two questions as having top priority. The first is: "What are the conditions for ignition and extinction?" and the second: "What are the reaction mechanisms and optimum conditions for most complete burnup?"

Division of the incinerator into two zones, Zone 1 being the fuel bed and Zone 2 being the overfire region of smoke and volatiles burnup, provides a modifier for the two questions, with priorities becoming *extinction* for the fuel bed, and *optimization* for the flame zone.

Four initial programs are planned to answer these questions:

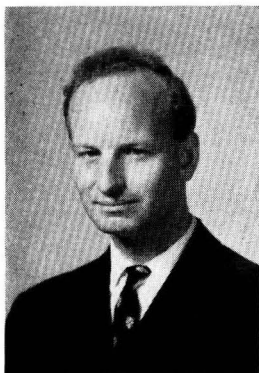
- Program A is a reactivity study of suspended paper spheres.
- Program B is a combustion pot

study of a packed bed of newspaper rolls or wooden dowels.

• Program C is a cold model study of mixing requirements for the overfire air with the objective of creating an ignition and flame holding zone.

• Program D is a study of a test incinerator designed to check the integrated conclusions from the other studies.

Progress has been made on implementation of the four programs, and further details of the progress will be made public when they are available.



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The author of many articles and publications on combustion and fuel technology, Dr. Essenhigh has been a frequent contributor to *Fuel*, *Combustion and Flame*, and *Industrial and Engineering Chemistry*. In addition to his teaching and research activities, Dr. Essenhigh is Examiner in Fuel Technology for the Pennsylvania professional engineers examination, and a consultant to industry in the area of furnace behavior, burner design, industrial combustion, and related topics. He is a member of Sigma Xi and Phi Lambda Upsilon, as well as the Combustion Institute, American Society of Mechanical Engineers, and other professional organizations.

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Stable Carbon Isotope Ratios as Indices of Petrochemical Pollution of Aquatic Systems

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■ Variations in the $^{13}\text{C}/^{12}\text{C}$ ratio of dissolved and particulate organic matter from several aquatic systems have been investigated. These measurements were made for natural and organic chemically polluted systems. $\delta^{13}\text{C}$ for natural systems ranges between -14 and -23 relative to the National Bureau of Standards isotope reference material No. 20. Petrochemical products and petrochemical effluents are much more depleted in ^{13}C , with a range from -25 to -49 . $\delta^{13}\text{C}$ of the dissolved organic matter was measured for 15 samples from the Houston, Tex., Ship Channel. Model calculations based on these data suggest that the $^{13}\text{C}/^{12}\text{C}$ ratio of dissolved organic matter may serve as a quantitative index of petrochemical pollution.

As a result of chemical isotope effects the various natural carbon reservoirs have different and somewhat characteristic values of the $^{13}\text{C}/^{12}\text{C}$ ratio (Craig, 1953). The carbon isotope ratios of several large carbon reservoirs are shown in Figure 1. The $\delta^{13}\text{C}$ notation is defined and discussed below. Biological reactions, in particular the photosynthetic fixation of inorganic carbon into organic carbon, are the major contributors to this isotope fractionation (Park and Epstein, 1960). In general, organic matter is enriched in ^{13}C with respect to inorganic carbon.

The study of these variations by petroleum geochemists has not only provided convincing evidence that petroleum is biological in origin, but has served as a means of relating a specific petroleum to a probable source rock (Silverman, 1967). Within a single organism different biochemicals may have different $\delta^{13}\text{C}$ values as a result of isotope effects in reactions leading to their synthesis (Abelson and Hoering, 1961). Indeed, these authors have shown that specific carbon

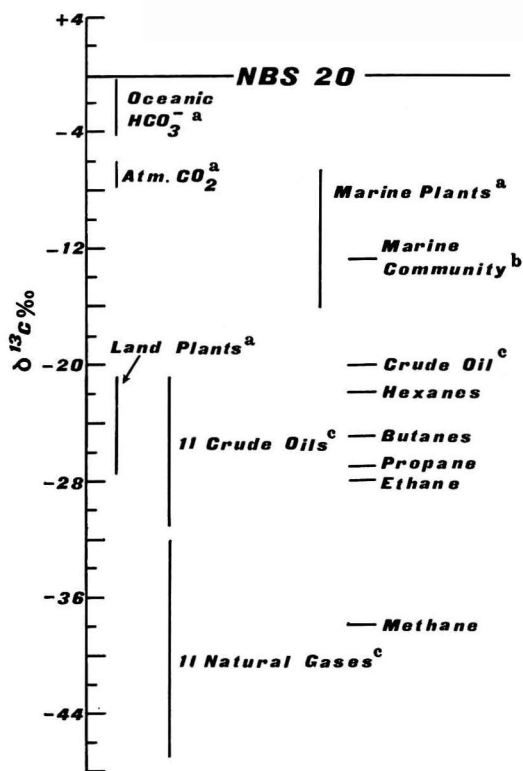


Figure 1. $\delta^{13}\text{C}$ of some carbon reservoirs

- a. Craig (1953)
b. Parker (1964)
c. Silverman (1967)

atoms within a single amino acid molecule may have a characteristic $\delta^{13}\text{C}$ value.

Friedman and Irsa (1967) have shown that air rich in automobile exhaust can show an 8 per mil enrichment in ^{12}C for the carbon dioxide. This shift toward a more negative $\delta^{13}\text{C}$ is due to the introduction of carbon dioxide derived from petroleum products. Using this natural tracer technique they show that for samples taken in the center of the business district in lower Manhattan approximately 20% of the CO_2 in the atmosphere at street level is produced by automobile exhaust. The fact that characteristic stable carbon isotope ratios persist in natural carbon reservoirs led the authors to investigate the possible use of these ratios in recognizing various sources of organic chemical pollution of water.

The aquatic system consisting of a marine bay receiving effluents from oil refineries and petrochemical plants seemed to be an ideal case for detailed study. Petroleum and natural gas have the most negative $\delta^{13}\text{C}$ of the various organic carbon reservoirs; marine organic matter has the least negative. The principle of the method then is simply that a mixture would have an intermediate value of $\delta^{13}\text{C}$. The exact value will depend on the $\delta^{13}\text{C}$ values of the normal and pollutant carbon, the organic carbon concentration of the normal water and effluent, and the magnitude of the volumes mixed. In principle, since all these variables can be related by an equation, one could calculate one variable from measured values of the others. The approach in this first study has been to try to establish general relationships among the variables rather than a detailed analysis of one marine system.

Rosen and Rubin (1964, 1965) described a parallel method for discriminating between natural and industrial pollution based on the ^{14}C activity of normal and fossil organic matter. Their ^{14}C method and our ^{13}C method are different in both principle and experimental technique, but they complement each other very well.

Experimental

Preparation of CO_2 . Soluble and particulate organic fractions were obtained by filtering 1- to 2-liter water samples through a glass filter pad (Gelman Type A). It was necessary to use a sample size that would yield 2 to 3 ml. of CO_2 . The filter pads, copper oxide, and iron pellets were placed in a clay cup for combustion in a radio-frequency furnace. This was connected to a vacuum line so that the evolved CO_2 could be condensed in a trap cooled with liquid nitrogen. The water containing the soluble organics was freed of inorganic carbon by acidification and flushing with nitrogen gas. The water plus a large excess of potassium persulfate was sealed in a 1- to 2-liter bulb under a slight vacuum and autoclaved for 1 hour at 123°C . Under these conditions the persulfate completely oxidizes the organic matter to CO_2 . The bulbs were attached to a vacuum line via a break seal. The seal was opened, and the CO_2 was distilled over and purified.

The amount of CO_2 was determined in both oxidation methods by manometry. A detailed description of the oxidation and purification techniques with regard to use in the preparation of CO_2 for isotope analysis will be published later.

Mass Spectrometric Measurements. The mass spectrometer was a 60° sector field, double collector instrument described by McKinney, McCrea, *et al.* (1950), designed to determine small differences in isotope ratios. The isotope analyses are expressed in terms of the parts per thousand (per mil) difference between the isotope ratio of the sample under investigation and the isotope ratio of a selected standard material.

$$\delta^{13}\text{C} = \frac{(^{13}\text{C}/^{12}\text{C}) \text{ sample} - (^{13}\text{C}/^{12}\text{C}) \text{ std.}}{(^{13}\text{C}/^{12}\text{C}) \text{ std.}} \times 1000$$

Thus samples enriched in ^{13}C relative to the standard will have positive values, whereas samples depleted in ^{13}C relative to the standard will have negative values. Negative samples are often referred to as "light." The standard for this work was the Solenhofen limestone (National Bureau of Standards isotope reference material No. 20). Samples were not corrected for O^{17} , since the correction is small when all samples and standards are equilibrated with the same tank oxygen. No inlet correction was required.

Sampling Plan. Three areas were sampled in detail: the Corpus Christi ship channel on which several small refineries are located, the Houston ship channel with its vast chemical complex, and a medium-sized petrochemical plant adjacent to a marine bay. In addition to these areas, samples were taken from several rivers, bays, and the Gulf of Mexico in order to establish a base line for normal concentration and $\delta^{13}\text{C}$ of aquatic organic matter.

The petrochemical plant, whose cooperation was obtained, provided a sample of feedstock gas and a variety of organic substances synthesized in the plant. $\delta^{13}\text{C}$ values for these substances are given, along with some reported earlier (Parker, 1967), in Table I. The petrochemical plant also allowed its effluent at several stages of purification to be sampled. The authors were thus able to follow $\delta^{13}\text{C}$ as intake river water flowed through the plant and emerged as treated effluent. This model system was very useful in planning sampling of the ship channels.

All water samples in this study were taken at the surface. Precautions were taken to prevent contamination. Samples were cooled with ice at the time of collection. The samples were filtered within a few hours after being returned to the laboratory. Once the filtered sample is sealed in the oxidation bulb it may be kept several days before being autoclaved; however, this was seldom done.

Results

Petrochemical Plant. The products of the petrochemical plant had approximately the same $\delta^{13}\text{C}$ as the starting materials (Table I). This is reasonable when one considers that

Table I. $\delta^{13}\text{C}$ of Materials from a Texas Petrochemical Plant

Date	Sample	$\delta^{13}\text{C}^a$
12-65	Natural gas master inlet	-30.7
12-65	Ethylene	-26.7
12-65	Propylene	-28.1
12-65	Acetylene	-24.9
12-65	High-density polyethylene I	-27.3
12-65	High-density polyethylene II	-29
12-65	Low-density polyethylene	-28.1
10-12-66	Styrene	-27.8
10-12-66	Cellosolve	-28.2
10-12-66	Ucon oil	-22.8
10-12-66	Monoethylene glycol	-29.3
12-65	2-Ethylhexanol	-30.5
12-65	Isobutyl alcohol	-26.9
12-65	Aromatic mixture	-30.7

^a $\delta^{13}\text{C}$ is in units of ‰ throughout this paper.

Table II. $\delta^{13}\text{C}$ and Concentration of Dissolved and Particulate Organic Matter for a Texas Petrochemical Plant

Date	Sample	DOM ^a		POM, ^b $\delta^{13}\text{C}$
		Mg. C/liter	$\delta^{13}\text{C}$	
8-23-66	River water intake	6.1	-18.5	-
8-24-66	River water intake	5.3	-19.0	-
8-24-66	River water intake	3.8	-16.6	-17.3 ^c
10-12-66	Stabilization pond	3100	-39.3	-31.2
8-23-66	1st oxidation pond	8.3	-33.3	-
8-23-66	2nd oxidation pond	11.4	-25.7	-
8-23-66	Barge canal	9.9	-14.4	-
1-5-67	Adjacent bay	3.0	-14.5	-
1-18-67	Adjacent bay	2.1	-23.6	-20.3
1-31-67	Adjacent bay	2.7	-18.8	-16.6
6-19-67	Gulf of Mexico	0.4	-20.6	-21.2

^a DOM, dissolved organic matter.

^b POM, particulate organic matter.

^c POM, 0.5 mg. per liter.

most of the reactions which transform the starting gases into products are carried out at high temperatures where isotope effects approach zero. Furthermore, the high per cent conversions sought by the industry would tend to lessen fractionation. There is some variation among the chemicals produced. This may be of interest to the plant operators who are knowledgeable about the conditions under which various reactions are carried out. Since the products retain the fairly negative $\delta^{13}\text{C}$, the effluent was expected to do so also. The data in Table II show that this is the case.

The raw effluent represented by the stabilization pond had a very negative $\delta^{13}\text{C}$ (-39.3) and a high dissolved organic matter (DOM) level. This effluent, diluted with fresh water, flows into the first oxidation pond. Here the amount of DOM is much lower, but the $\delta^{13}\text{C}$ value (-33.3) indicates that most of this DOM is petrochemical. By the time the effluent reaches the second oxidation pond the $\delta^{13}\text{C}$ is down to -25.7,

still in the range of petroleum but clearly depleted in petrochemical carbon. The barge canal which receives the final effluent from the second oxidation pond had a normal $\delta^{13}\text{C}$. The adjacent bay, of which the barge canal is actually a part, may be considered to represent normal aquatic $\delta^{13}\text{C}$ for this system. The consistent relationships shown by these data are really better than one would expect from such a small sampling effort. The data give rise to two important questions: What is a normal value for $\delta^{13}\text{C}$ of DOM and particulate organic matter (POM) in an aquatic system, and what is the mechanism by which the very negative effluent becomes more positive as it flows through the oxidation pond treatment system?

An exact number for a normal $\delta^{13}\text{C}$ of an aquatic system cannot be given. There is a certain amount of variation in a nonpolluted natural system. One must be satisfied with ranges; however, the ranges are fairly narrow. The values given in Table II (-14.4 to -23.6) represent the extreme range. A one-year study of this river-bay system has shown that -16 to -21 is the most probable range. Based on these relatively few measurements of $\delta^{13}\text{C}$ of DOM and POM one cannot be sure as to what extent large aquatic systems vary in their normal ranges. The Gulf of Mexico waters fall in a narrow range. It would be very useful and interesting to compare other large aquatic systems.

The main mechanism by which the very negative effluent becomes less negative appears to be chemical and biological oxidation of the petrochemical carbon to CO_2 . This light CO_2 then undergoes isotopic exchange with the more positive CO_2 of the atmosphere. This CO_2 will be isotopically similar to normal aquatic CO_2 . The new DOM and POM being made by the plants will be based on this carbon and will show a near-normal $\delta^{13}\text{C}$. Dilution with fresh water containing normal DOM will have the same result but will require very large volumes of water.

Corpus Christi Ship Channel. The very negative $\delta^{13}\text{C}$ carbon found in the petrochemical plant is absent from this system. The refinery effluent sampled just before it flows into the ship channel contained 33.5 mg. per liter of DOM with a $\delta^{13}\text{C}$ of -24.6. This represents approximately the most negative carbon this system is receiving. The data in Table III show no definite trend. The main problem is that one cannot state a narrow range for normal carbon for this system. This system is receiving more detailed study, but it will be necessary to allow the effects of the 1967 hurricane to wear off. There is a relatively small chemical complex at this location. The authors plan to establish a base line now, so that as the area grows even a small change in the $\delta^{13}\text{C}$ of the aquatic carbon reservoirs can be detected.

Houston Ship Channel. The data in Table IV indicate that the DOM and POM of this system are rich in petrochemical carbon. This applies to sample 12, which is in the San Jacinto River, and to samples 16 and 17, which are well into

Table III. $\delta^{13}\text{C}$ and Concentration of Dissolved Organic Matter from the Corpus Christi Ship Channel

Date	Sample ^a	Mg. C/Liter	$\delta^{13}\text{C}$
11-5-66	A	2.7	-16.5
11-5-66	B	2.9	-22.4
11-5-66	C	5.7	-16.7
11-5-66	D	3.6	-18.7
5-3-67	E	1.5	-21.5
5-3-67	F	3.3	-18.7
12-5-66	G	2.4	-15.4
12-5-66	H ^b	33.5	-24.6

^a See Figure 2 for locations.
^b Refinery effluent.

Galveston Bay. Again one cannot be sure of an exact base line. But if the range of -16 to -21, found for a similar but nonpolluted river-bay system, is accepted, the trend is clear. The samples in this study represent the channel water, not the effluent of various plants. The channel receives the effluent from sewage treatment plants and a paper mill in addition to petroleum-based plants. The sewage probably would tend to push the $\delta^{13}\text{C}$ in a less negative direction relative to the petrochemicals. Paper mill effluent had a DOM $\delta^{13}\text{C}$ value of -27 in the case of an east Texas mill, based on a single unpublished measurement made by the authors.

When normal and pollutant carbon are mixed, the $\delta^{13}\text{C}$ of the mixture is given by the expression:

$$\delta_m = \frac{C_n\delta_n + C_p\delta_p}{C_n + C_p} \quad (1)$$

where C = concentration of carbon, mg. per liter
 δ = $\delta^{13}\text{C}$

n refers to normal carbon, p to pollutant carbon, and m to the mixture carbon.

Since only the ratio of amount of pollutant to normal carbon in the mixture is of interest, rearrangement gives

$$\frac{C_p}{C_n} = \frac{\delta_n - \delta_m}{\delta_m - \delta_p} \quad (2)$$

Although there is a good deal of uncertainty in δ_n and δ_p , some model calculations are of interest. A value of -20 for δ_n is realistic, although probably at the negative end of the range. The average of all the DOM data for the system, -30.5, is a suitable value for δ_m . If δ_p is taken as -39, which is the value of the untreated plant effluent from Table II, C_p/C_n is 1.19. This would indicate that better than half of the DOM of the system is derived from pollution. Taking δ_p as -32, which is the value of one plant effluent just as it goes into the channel, C_p/C_n is 7. In systems where δ_n is the same as

Table IV. $\delta^{13}\text{C}$ and Concentration of Dissolved and Particulate Organic Matter in the Houston Ship Channel^a

Station ^b	DOM		POM	
	Mg. C/liter	$\delta^{13}\text{C}$	Mg. C/liter	^{13}C
1	5.8	-26	20	-19.8
2	5.6	-31.2	4.2	-21.3
3	3.9	-31.5	3.2	-24.2
4	4.0	-29.3	2.6	-23.1
5	9.0	-30.1	19	-26.3
6	26	-26.9	12	-24.4
7	3.1	—	4.0	-23.3
8	11	-48.8	8.8	-27.4
9	3.8	-29	2.4	-24.7
10	8.4	-27.1	3.8	-25.9
11	6.0	-27.5	2.9	-24
12	4.1	-28.2	3.6	-25.2
13	2.7	-28.2	4.0	-26
14	19	-32	16	-25.8
15	2.9	—	2.2	-23.0
16	1.4	-24.8	2.7	-23.3
17	2.1	-24.9	4.4	-21.1

^a All samples taken 10-13-67.
^b Refer to Figure 2 for location of stations.

δ_p this calculation yields no useful information. Rosen and Rubin (1965) found with the ^{14}C method that between 50 and 95% of the DOM of a river water was derived from industrial pollution.

One can do a similar calculation for the POM. DOM seems to be a more usable parameter, perhaps because it is more evenly distributed in water.

Discussion

The studies described are the test of the idea that stable isotope ratios may serve as a useful index of organic pollution of aquatic systems. The data suggest that this is the case. It is the method, its evaluation, and possible extension which were of concern at this point rather than the state of a particular aquatic system.

More measurements are needed on normal aquatic systems to be able to state a normal $\delta^{13}\text{C}$ with a minimum range. The variations in $\delta^{13}\text{C}$ values are natural variations of the system. The experimental error is less than ± 0.5 per mil. Once suitable background data are obtained for various systems it will not be necessary to remeasure them constantly. Isotope ratios tend to stay fairly constant. Any long-term drift in ratios probably will indicate a major change in the carbon cycle. Unlike the $^{14}\text{C}/^{12}\text{C}$ ratio, small additions or removal of carbon will not shift the $^{13}\text{C}/^{12}\text{C}$ ratio. Measurements of $\delta^{13}\text{C}$ of the raw effluent of a variety of industrial plants would greatly aid in evaluating measurements on natural waters.

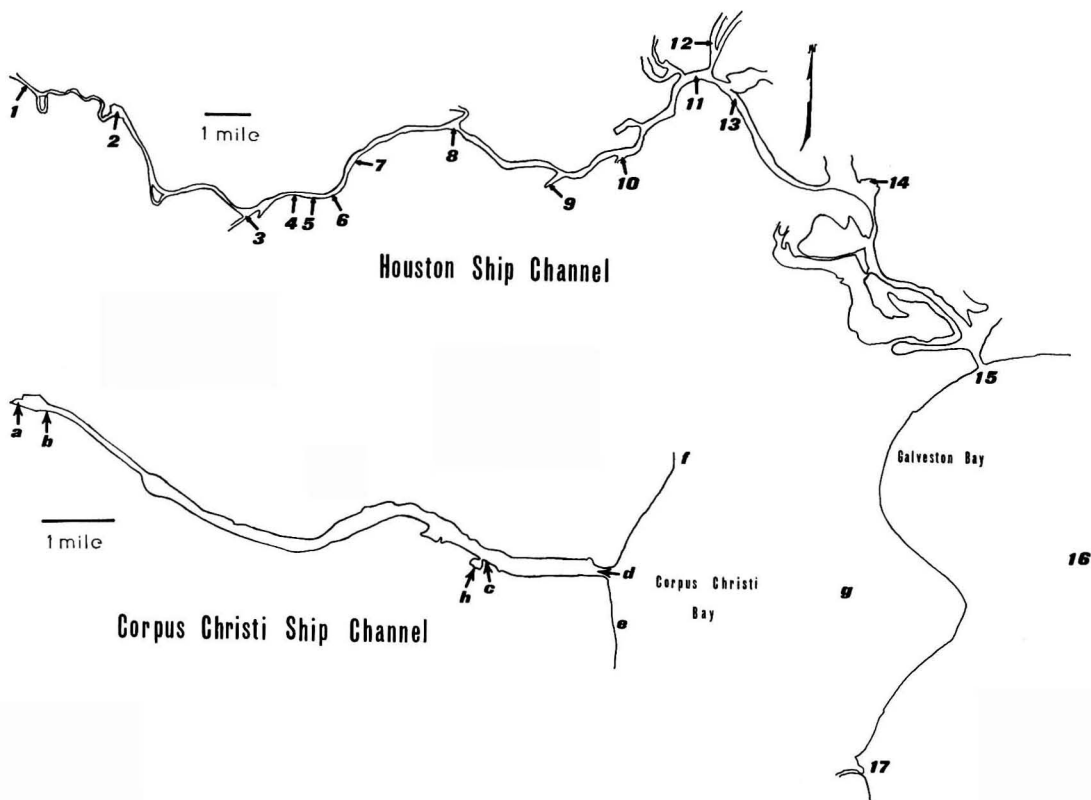


Figure 2. Location of sampling stations on Houston and Corpus Christi, Tex., ship channels

Other types of pollution may be studied via isotope ratios. Sewage is of particular interest because it is so abundant and rich in DOM. Other stable isotope pairs such as $^{15}\text{N}/^{14}\text{N}$ or $^{34}\text{S}/^{32}\text{S}$ may be useful. Finally, the $\delta^{13}\text{C}$ method gives no information about the chemical structure of organic pollution or its toxic properties. It appears to be useful for gaining some insight into the over-all carbon flux of large systems from relatively few and simple measurements.

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Ion Exchange Equilibria. Chloride-Phosphate Exchange with a Strong Base Anion Exchanger

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■ The ion exchange characteristics of various chloride-phosphate mixtures were studied on a strongly basic anion exchanger. The electroselectivity principle is applicable to this system, and the resin selectivity for phosphate increases as either the absolute or the relative amount of phosphate decreases. The phosphate species exchanged from solutions of pH 7.5 to 9 is the HPO_4^{-2} ion.

During a study conducted in this laboratory dealing with the removal of phosphates from water with ion exchange materials, a knowledge of quantitative selectivity data was needed. A number of studies have been made to test the effectiveness of anion exchangers for the removal of phosphates from sewage plant effluents (Eliassen, 1963; Eliassen and Wyckoff, 1964; Martinez, 1962). While these studies demonstrated that ion exchangers would remove phosphates and, thus, were potentially useful, no systematic study of selectivities was made. Since data of the type desired were not available, this study was conducted to determine selectivity coefficients for the exchange of phosphate in the presence of chloride ions.

Experimental

The ion exchanger used was Bio-Rad AG1-X4 (20- to 50-mesh), a strongly basic polystyrene resin. This material, supplied in a purified form, was further conditioned by treatment, alternately, with sodium hydroxide and hydrochloric acid (with intermediate water rinsing); usually, the resin was put through six cycles, finishing with the resin in the chloride form. All water used was doubly distilled and all reagents were carbon dioxide free.

The exchange studies were carried out using a small amount of resin (about 1 gram in the chloride form) in a jacketed column of 10 mm. I.D., maintained at $25 \pm 0.02^\circ \text{C}$. A large excess of the appropriate chloride-phosphate solution was passed through the column at a flow rate of 0.5 ml. per minute. Equilibrium was considered to be obtained when the effluent pH was constant and equal to that of the inflowing solution.

Chloride was determined by potentiometric titration using a silver chloride electrode. Phosphate was measured spectrophotometrically using the method of Murphy and Riley (1962).

The resin capacity (3.91 meq. per gram of dry resin) was obtained by titration of the hydroxide form of the resin with standard hydrochloric acid (Helfferich, 1962).

The water content of the resin (25.96%) was obtained by allowing weighed portions of resin in the chloride form to come to constant weight over P_2O_5 in a desiccator for eight days.

Four series of solutions of differing total normality were prepared by mixing appropriate amounts of NaCl and Na_2HPO_4 solutions. Phosphate normalities were computed assuming that the phosphate species present in solution and undergoing exchange was HPO_4^{-2} ; thus, the phosphorus normalities are twice the molarities in both the solution and resin phases. It was further assumed that, since the solutions are dilute, molarity is an adequate measure of molality.

The four series of solutions were 0.0075, 0.010, 0.025, and 0.050 in total normality; within each series the equivalent ionic fraction of phosphate, X_P , was adjusted to 0.1, 0.3, 0.5, 0.7, and 0.9.

The charge, n , on the exchange phosphate species was determined by measuring the number of moles of chloride exchanged per mole of phosphate exchanged. Values of n were obtained in two ways.

The chloride and phosphate concentrations of the solutions to be passed through the resin were obtained by analysis. The resin was in the chloride form at the start of the exchange. As the chloride-phosphate solution passed through the resin bed, the phosphate concentration of the influent would be diminished (ΔP), while that of chloride would be increased (ΔCl) by an equivalent amount. If phosphate is exchanged as the HPO_4^{-2} ion, then the ratio $\Delta Cl/\Delta P$ will be two.

After equilibration of the system, the resin was returned to the chloride form by treatment with hydrochloric acid. In this regeneration process, the phosphate is removed from the resin and appears in the effluent, while an equivalent amount of chloride disappears from the solution. A measured amount of standard acid was used, and the phosphate concentration and change in chloride concentration were determined. Again, $\Delta Cl/\Delta P$ values were calculated.

Using the above methods for the 19 solutions tested, an average value of $n = 1.99$ was obtained. Thus, the exchanged species definitely is the HPO_4^{-2} anion.

Calculations

The expressions used to calculate certain quantities of interest are given below.

Practical (molal) selectivity coefficient

$$K_{ClP} = \frac{\bar{m}_P^{|Z_{Cl}|} m_{Cl}^{|Z_P|}}{m_P^{|Z_{Cl}|} \bar{m}_{Cl}^{|Z_P|}}$$

Table I. Selectivity Coefficients and Related Quantities

X_P	$10^3 K_{Cl}^P$	${}^N K_{Cl}^P$	α_{Cl}^P	\bar{X}_P/\bar{X}_{Cl}	$\bar{m}_P/m_P \times 10^{-2}$
0.0075 Total Normality					
0.1	9.53	19.9	7.32	1.07	56.4
0.3	3.18	4.71	2.92	1.26	26.8
0.5	2.74	3.74	2.42	2.76	21.3
0.7	2.75	3.94	2.20	4.68	17.5
0.9	34.0	54.9	7.95	57.8	15.9
0.010 Total Normality					
0.1	6.18	5.55	4.94	0.51	39.4
0.3	3.96	3.64	2.94	1.06	21.9
0.5	2.65	2.47	2.04	1.81	15.7
0.7	3.17	3.36	2.01	4.62	12.8
0.9	10.1	10.8	3.42	25.3	11.6
0.025 Total Normality					
0.1	7.28	3.08	2.71	0.31	10.1
0.3	6.10	2.96	1.97	0.93	6.38
0.5	3.79	1.63	1.39	1.37	5.14
0.7	4.88	2.31	1.49	3.72	4.58
0.9	2.26	1.02	0.97	8.71	4.19
0.050 Total Normality					
0.3	5.81	1.27	1.18	0.54	2.41
0.5	4.05	0.82	0.93	0.88	2.16
0.7	4.97	0.92	0.99	2.66	1.97
0.9	2.04	0.40	0.67	5.17	2.22

Table II. Chloride-Phosphate Exchange Data for AGI-X4

X_P	Solution ^a		Exchange ^b	
	Cl	P	Cl	P
0.050 Total Normality				
0.306	35.3	7.76	1.16	0.588
0.504	25.4	12.9	1.58	0.876
0.701	15.2	17.8	2.48	1.10
0.894	5.41	22.8	2.86	1.60
0.025 Total Normality				
0.102	22.5	1.28	0.780	0.407
0.299	17.6	3.76	1.63	0.756
0.495	12.6	6.19	1.96	1.00
0.700	7.63	8.91	2.69	1.29
0.896	2.63	11.3	3.07	1.50
0.010 Total Normality				
0.102	9.15	0.522	0.565	0.314
0.302	7.22	1.56	0.865	0.516
0.503	5.10	2.58	1.08	0.618
0.697	3.09	3.55	1.38	0.692
0.882	1.22	4.56	1.62	0.809
0.0075 Total Normality				
0.100	6.92	0.382	0.869	0.328
0.293	5.34	1.11	0.933	0.452
0.496	3.83	1.88	1.16	0.614
0.683	2.42	2.61	1.38	0.697
0.881	0.905	3.34	1.65	0.821

^a Values are given as 10^3 moles-liter⁻¹ initial concentration; resin is in chloride form.
^b Values are given as 10^3 moles; values represent amount of chloride lost by resin upon uptake of phosphate by resin.

Rational selectivity coefficient

$${}^N K_{Cl}^P = \frac{\bar{X}_P^{Z_{Cl}} X_{Cl}^{X_P}}{\bar{X}_P^{Z_{Cl}} \bar{X}_{Cl}^{X_P}}$$

Separation factor

$$\alpha_{Cl}^P = \frac{\bar{m}_P m_{Cl}}{m_P \bar{m}_{Cl}}$$

In the above expressions, m and \bar{m} are the molality of the subscripted species in solution and in the resin, respectively; X and \bar{X} are the respective equivalent ionic fractions, defined as

$$X_P = \frac{\text{equivalents of P}}{\text{equivalents of P} + \text{equivalents of Cl}}$$

and $X_{Cl} = 1 - X_P$. The charges on the phosphate and chloride ions, respectively, are Z_P and Z_{Cl} .

In addition to the above three quantities, the ratios \bar{X}_P/\bar{X}_{Cl} and \bar{m}_P/m_P were calculated.

Results and Discussion

Values for the several quantities calculated are shown in Table I. The charge on the phosphate species was two for these calculations. The experimental data used for calculating the quantities shown in Table I are given in Table II.

In Figure 1, the molality ratio of resin phosphate to that

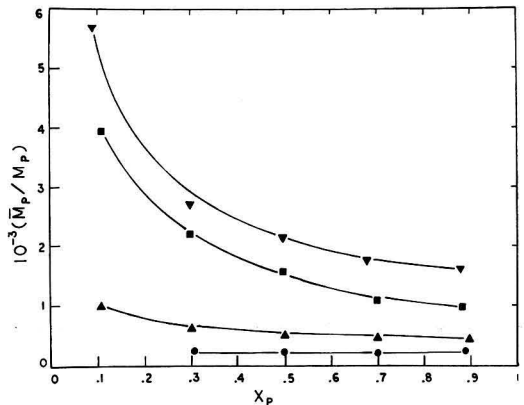


Figure 1. Molality ratio, \bar{m}_P/m_P , as a function of equivalent fraction of phosphate, X_P

Total normalities: ●, 0.05; ▲, 0.025; ■, 0.01; ▼, 0.0075

remaining in solution has been plotted as a function of the equivalent ionic fraction of phosphorus in the original solution, X_P . For any given molality (except perhaps the 0.050 case) the proportion of the total phosphorus found in the resin phase increases as X_P decreases. Also, for any given value of X_P , the proportion of total phosphorus in the resin phase increases as the absolute concentration decreases. Thus, the selectivity of the exchanger for phosphorus increases as either the relative or the absolute amount of phosphorus in the equilibrating solution decreases. This demonstrates that the electroselectivity principle—i.e., an ion exchanger prefers the ion of higher charge, and this preference increases with increasing dilution—may be applied to chloride-phosphate systems.

Figure 2, in which the separation factor, α , is plotted against X_P of the original solution, illustrates a behavior similar to that noted in Figure 1. That is, the relative amount

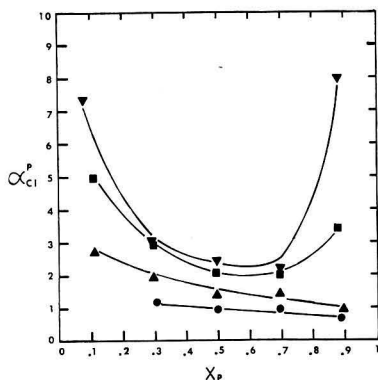


Figure 2. Separation factor, α_{Cl}^P , as a function of equivalent fraction of phosphate

Total normalities: ●, 0.05; ▲, 0.025; ■, 0.01; ▼, 0.0075

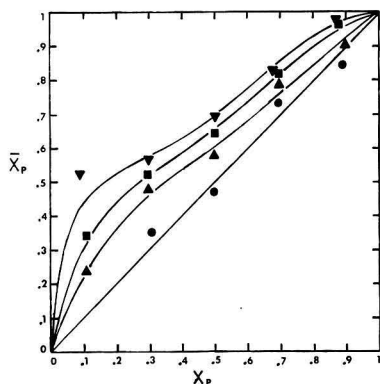


Figure 3. Equivalent fraction of sorbed phosphate as a function of the equivalent fraction of phosphate in solution

Total normalities: ●, 0.05; ▲, 0.025; ■, 0.01; ▼, 0.0075

of phosphate exchanged increases upon decreasing either the total normality or the equivalent ionic fraction of phosphate. The separation factor goes through a minimum for the 0.010 and 0.0075 normal systems; the increased factors for high values of X_P are probably the result of mass action effects, whereas those for low values of X_P are due to electroselectivity.

In Figure 3, the equivalent ionic fraction of phosphate in the resin phase is shown as a function of that in solution at equilibrium. One would expect that, if the resin showed no selectivity for either chloride or phosphate, a line of unit slope would result—that is, the distribution of chloride and phosphate would be the same in the resin as in the solution. This is essentially the case for the 0.050N systems. As the total normality is decreased, however, the curves show a progressively greater positive deviation from unit slope. Since the deviation is a positive one, the phosphate is more selectively exchanged. Further, the greater deviations occur when X_P is small, which corroborates the conclusion that the selectivity for phosphate tends to be higher when X_P is low.

Conclusions

From the results obtained in this work it seems that the electroselectivity principle is applicable to the removal of phosphates from water using ion exchange techniques, when the competing ions behave as does chloride. An important question relating to the success of phosphate removal from water is whether the exchanger will be sufficiently selective toward phosphate to enable its exchange, even in the presence of large amounts of competing ions. The results of this study indicate that the resin becomes more selective for phosphate as either the relative or the absolute amount of phosphate decreases. This is particularly important for the removal of pollutant phosphate from a water supply, for example. If the phosphate concentration is high, an ion exchanger will probably remove phosphate; however, as the phosphate concentration decreases, its concentration relative to other ions present becomes small. These results indicate that the selectivity of the exchanger for phosphate should increase, rather than decrease, as phosphate is removed.

While the ultimate test of the efficacy of ion exchangers in removing phosphates from natural waters would require a field test, this study strongly suggests that such a test could be made with a reasonable chance of success. In the solution with $X_P = 0.1$ and a total normality of 0.0075, the phosphate was reduced from about 12 p.p.m. of P to less than 0.01 p.p.m., even in the presence of a ninefold excess of chloride initially.

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Biodegradation of Nitrilotriacetic Acid in Aerobic Systems

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■ The biodegradation of nitrilotriacetic acid in the biochemical oxygen demand test and laboratory activated sludge units has been investigated. Nitrilotriacetic acid was degraded with acclimatized bacterial populations in both the biochemical oxygen demand test and activated sludge. A one-week acclimatization period was needed in the activated sludge units.

The apparent accelerated rate of eutrophication of lakes and streams has been receiving increased public attention because of the obnoxious algal and higher aquatic plant blooms observed in these waters. These blooms have frequently been associated in some way with the discharge of municipal or industrial wastes. Frequently, the phosphorus in these waste waters is alleged to be one of the principal causes of many eutrophication problems. Since a significant part of the phosphorus in municipal and some industrial wastes is derived from detergents, consideration is being given to finding a compound that may be used to substitute for the condensed phosphates used in detergent formulations. One of the compounds that may be used is the trisodium salt of nitrilotriacetic acid, NTA (*Chem. Eng. News*, 1967; Pollard, 1966).

Since NTA is a strong complexing agent, questions may be raised about its possible effects on water and waste treatment processes and aquatic life. Therefore, one of the first questions to be raised is its biodegradability. Pollard (1966) states that the evidence for NTA biodegradability is inconclusive and contradictory, and that the biochemical oxygen demand, BOD, of NTA appeared to be insignificant over a 31-day period. He did not present any data to support these statements. Recently, Swisher, Crutchfield, *et al.* (1967) have reported that NTA is biodegradable in both batch and continuous activated sludge units. Pfeil (1967) has presented a literature review on the biochemical and complexing characters of NTA.

This paper reports on a study of the biodegradability of NTA by the BOD test and in laboratory activated sludge units.

Experimental Procedures and Materials

Reagents. A nitrilotriacetic acid stock solution was prepared by suspending 5.0 grams of NTA (item No. 5417; lot No. 6620, Eastman Organic Chemicals, Distillation Products Industries) in 250 ml. of distilled water. This suspension was dissolved by neutralizing with reagent grade sodium hydroxide to a pH

of 7.0 ± 0.1 using a Beckman Model H-2 glass electrode pH meter. All other chemicals used were ACS reagent grade or better. Distilled water was used to prepare solutions of other reagents.

Determination of NTA. The titration method of Cihalik and Novak (1956) for the determination of Complexon I (NTA) was used. The NTA was titrated by a copper salt in the presence of sodium acetate (AcONa) without indicator or using catechol violet or murexide as an indicator. A standard copper solution (1 ml. = 1 mg. of copper), AcONa (10% w./v.), and murexide (0.1% w./v.) solutions were prepared and used to titrate the standard NTA solution (1 ml. of copper = 3 mg. of NTA). This titration procedure was used to determine the concentration of NTA in the activated sludge units.

Acclimation of Seed Organisms. Since NTA is a synthetic organic compound and would not likely be found in naturally occurring materials, an attempt was made to see if it would be necessary to acclimatize sewage organisms to this compound so that they could utilize it as a source of energy. Small, batch-type activated sludge units consisting of 2-liter separatory funnels were set up and seeded with activated sludge (1 liter of activated sludge plus 1 liter of raw sewage). These units were kept at room temperature and were supplied with unfiltered compressed air from the laboratory compressed air system. Once or twice a day the air supply to the units was shut off and the activated sludge floc was allowed to settle for 10 to 15 minutes. Five hundred milliliters of the supernatant liquid was removed and replaced with 500 ml. of raw sewage and the air supply turned on again. Unit A was used as a control. In Unit B, increasing amounts of NTA solution were added to the 500-ml. portion of raw sewage before being added to this activated sludge unit. The concentration of NTA in the raw sewage was increased on successive days from 10 mg. per liter to a maximum of 100 mg. per liter and the dosage was maintained at this level. Acclimated seed organisms for biochemical oxygen demand and oxygen uptake determinations were obtained from this source. No change in settling characteristics of the sludge was observed as a result of adding NTA.

The raw sewage and activated sludge were obtained either from Nine Springs Treatment Works, Madison, Metropolitan Sewerage District, Madison, Wis., or from the small experimental activated sludge pilot plant located in the Civil Engineering Building, Randall Ave., University of Wisconsin, Madison, Wis.

Biochemical Oxygen Demand. The general procedure for the biochemical oxygen demand (BOD) determination was followed as outlined in Standard Methods for the Examination of Water and Wastewater (A.P.H.A., 1965). The concentration of NTA was varied in the BOD bottles and ranged from 0 to 320 mg. per liter. Either raw sewage that had been

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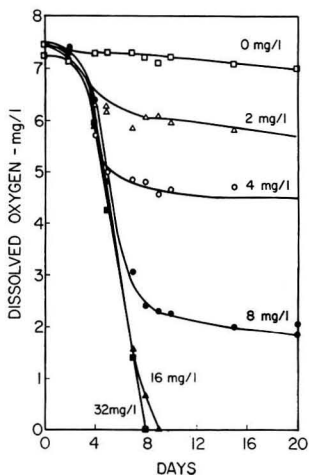


Figure 1. Dissolved oxygen remaining in BOD bottles containing NTA in standard dilution water with acclimated seed

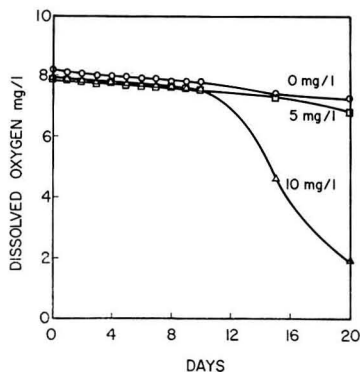


Figure 2. Dissolved oxygen remaining in BOD bottles containing NTA in standard dilution water with nonacclimated seed

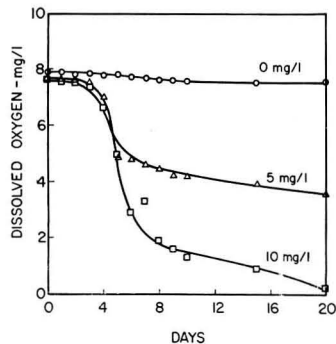


Figure 3. Dissolved oxygen remaining in BOD bottles containing NTA in standard dilution water with acclimated seed

kept at room temperature for 24 hours in an open container (aged seed), or activated sludge (unit A) was used as the source of the nonacclimated seed organisms. The activated sludge exposed to NTA (unit B) was used as the source of the acclimated seed organisms. This sewage was filtered through several layers of cheesecloth to remove the large particles and obtain a fairly homogeneous seed culture prior to adding it to the standard BOD dilution water. The BOD bottles were stored in the dark in a 20° C. thermostatically controlled air incubator until removed for titration of the residual oxygen.

Total Suspended Solids. The total suspended solids or mixed liquor suspended solids (MLSS) of the activated sludge units were determined by filtering, with the aid of a water aspirator, 25 ml. of the sample through a tared fiber-glass mat in a Gooch crucible. The difference between the tare weight and weight of filtered sample after drying for one hour at 103–105° C. was used to determine the total suspended solids in the aeration chamber.

Results

BOD Experiments. Since the purpose of this study was to determine the biodegradability of NTA, emphasis in the experimental work was first placed on the BOD of this compound.

An exploratory set of BOD experiments were set up to determine the 5-day BOD of NTA. Increasing concentrations of NTA in standard synthetic BOD dilution water containing aged sewage as source of seed organisms were prepared and placed in standard 300-ml. BOD bottles. The concentration of NTA ranged from 0 to 320 mg. per liter. The 5-day BOD value of NTA, average of three results, was negligible under conditions of this experiment.

The BOD determination was then repeated at concentrations of 20 and 100 mg. per liter of NTA to compare the aged sewage seed with seed obtained from unit B which had been exposed to increasing amounts of NTA during the previous week. The data for this experiment (Table I) show that by the 13th day of incubation, the BOD bottles that contained the

seed organisms previously exposed to NTA had completely depleted the available oxygen. The aged sewage seed organism had not been able to utilize the NTA in the sample and had not significantly depleted the available oxygen in 30 days of incubation.

The BOD determination was again utilized to determine the oxygen requirement for the degradation of NTA by acclimated seed organisms. The concentration of NTA varied from 0 to 32 mg. per liter. The results are presented in Figure 1. There appears to be a lag period of a few days before the degradation of NTA occurs. At the two higher concentrations of NTA, the available oxygen in the BOD bottle was depleted by the eighth and ninth day of incubation. The 20-day value for the 4 mg. per liter concentration appears out of line with the rest of the results and cannot be explained.

To confirm the results of the experiments discussed above, additional BOD experiments were conducted. The source of nonacclimated seed organisms was activated sludge unit A,

Table I. Degradation of NTA by Seed Organisms from Two Different Sources

No. of Days Incubation	Dissolved oxygen, mg./L., remaining in BOD bottles ^a					
	Aged Sewage Seed Organisms, Mg./L. NTA			Prior Exposure of Seed Organisms to NTA, Mg./L. NTA		
	0	20	100	0	20	100
0	7.55	7.55	7.1	7.6	7.35	6.85
5	7.2	7.4	6.85	7.35	7.1	6.75
11	7.0	7.25	6.8	7.05	0.05	3.5
13	7.1	7.2	6.55	7.05	<0.05	<0.05
15	7.1	7.3	6.6			
20	7.0	6.95	6.4			
24	7.1	7.10	6.5			
30	6.2	5.5	5.7			

^a Results from single determinations.

and the acclimated seed organisms were obtained from activated sludge unit B. The concentration of NTA was 5 mg. per liter and 10 mg. per liter and a control containing 0 mg. per liter. The results of this experiment are presented in Figures 2 and 3. No obvious degradation of NTA by the nonacclimated seed organisms was observed after 20 days' incubation at 5 mg. per liter. The acclimatized seed organisms were able to degrade the NTA following a lag period of three days, confirming the results of the previous experiment. The apparent oxygen utilization by the nonacclimated seed organisms in the 10 mg. per liter of NTA concentration on the 15th and 20th day of incubation may possibly be due to the development of some acclimatized organisms to NTA.

Acclimation of Seed Organisms. An activated sludge aeration cylinder unit C, similar to the other two units, was set up with 1 liter of activated sludge obtained from the activated sludge aeration tank at the Civil Engineering Building and 1 liter of raw sewage. At approximately 12-hour intervals thereafter, the air supply was shut off for 10 to 15 minutes to allow the activated sludge solids to settle, 500 ml. of supernatant liquid was removed and replaced with 500 ml. of raw sewage containing NTA. The concentration of NTA in the raw sewage was increased daily, and after the first day, the concentration of NTA in the aeration cylinder was determined by the titration procedure before and after the addition of the raw sewage containing the NTA. The mixed liquor suspended solids (MLSS) was about 1760 mg. per liter for this experiment.

The results are plotted in Figure 4. The vertical line represents the amount of NTA that was added with the raw sewage. The slanted line represents the degradation of NTA accomplished by the acclimatized organisms over the 12-hour period between additions of NTA. The results show that up to the fifth day very little degradation of NTA occurred. From the fifth to the seventh day organisms had developed that were able to degrade rapidly the added NTA. They were able to handle loadings as high as 110 mg. per liter without any adverse effect.

To ascertain if the absence of NTA in the raw sewage had any effect on the ability of the acclimated organisms to degrade NTA, raw sewage that was fed to the activated sludge units from two to five days contained no NTA. The results of the degradation of NTA in these units is presented in Figures 5, 6, and 7.

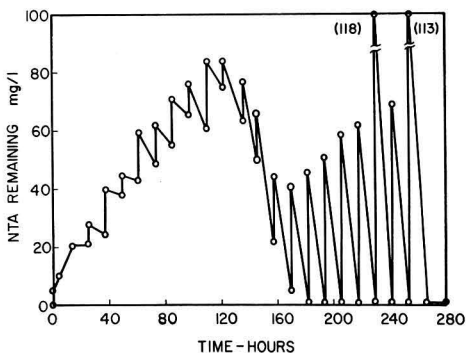


Figure 4. Activated sludge unit C, development of acclimated organisms to NTA

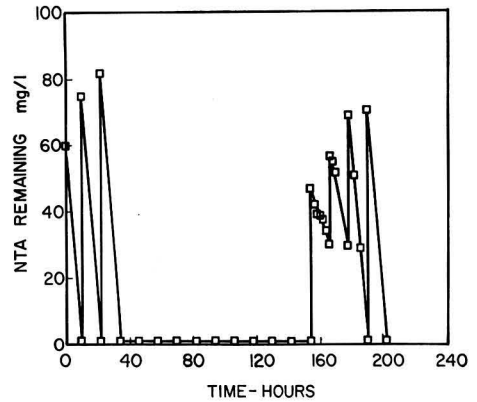


Figure 5. Activated sludge unit C, containing organisms, acclimated to NTA

NTA degradation before and after 5 days' absence of NTA raw sewage feed

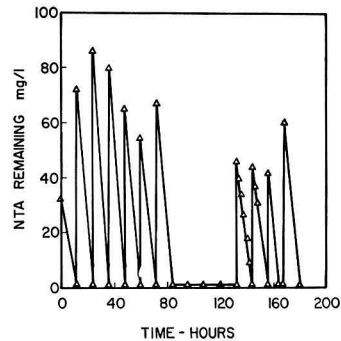


Figure 6. Activated sludge unit B, containing organisms acclimated to NTA

NTA degradation before and after 2 days' absence of NTA in raw sewage feed

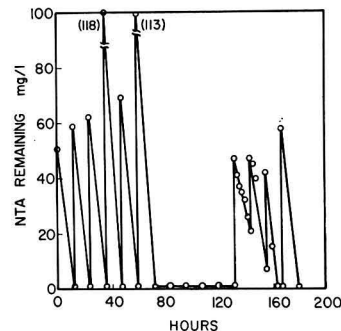


Figure 7. Activated sludge unit D, containing organisms acclimated to NTA

NTA degradation before and after 2.5 days' absence of NTA in raw sewage feed

For unit C (Figure 5), the five days of absence of NTA in the raw sewage had an adverse effect on the acclimated organisms in their ability to degrade NTA. Almost two days of continuous exposure to NTA was required before the organisms were again acclimated and could readily degrade NTA. For unit B (Figure 6) a two-day absence of NTA had no apparent adverse effect on the ability of the acclimated organisms to degrade NTA dosages within a 12-hour period. Another aeration unit (unit D) similar to unit C was set up and acclimated to NTA. For unit D (Figure 7) two and one-half days' lack of NTA in the raw sewage had a slight adverse effect on the acclimated organisms. A little more than one day was required before the organisms were again acclimated.

Discussion

Degradation of NTA. The data show that NTA can be biologically degraded following a period of acclimation of the organisms to this compound. A period of about one week under laboratory conditions is needed for the organisms to become acclimatized to accept this compound as a source of energy after initial and continuous exposure to it. After acclimatization this compound can be readily degraded.

Although the concentrations of NTA used in these experiments were probably somewhat higher than would be expected in municipal sanitary wastewater, the results indicate that organisms in the secondary treatment facilities would be able to degrade this compound about one week after initial exposure.

The acclimated organisms appear to be able to withstand up to a two-day starvation period without NTA with no adverse effect on their ability to degrade this compound. If this period is two and one-half days or greater, a certain length of time would be required for the organisms to again become adapted to degrading NTA. This period of acclimation would depend on the length of time that the organisms were without NTA and could extend up to seven days which was the original length of time for the acclimatization of the organisms.

Oxygen Requirement of NTA. The results of the BOD determinations also indicate that NTA is biodegradable as shown by the oxygen utilization by the acclimated organisms in the process of degrading this compound. In the BOD determination there appears to be a lag period of about three days before there is a significant increase of oxygen utilization. A summary of the oxygen requirement of NTA at various concentrations is presented in Table II.

The results show that the oxygen requirement of NTA varied from 0.61 to 0.72 mg. per liter of oxygen per milligram per liter of NTA at the end of 20 days. The average value was 0.67 mg. per liter of oxygen per milligram per liter of NTA. This value is slightly higher than the experimental value obtained by the chemical oxygen demand (COD) value of 0.65 mg. per liter of oxygen per milligram per liter of NTA. The value obtained by the BOD determination could be expected to be slightly higher than the COD determination since organisms are better able to utilize the acetic acid radical in NTA in the oxidation process, whereas the carbonaceous portion of this compound appears to be incompletely oxidized by the acid-dichromate procedure of the COD determination.

The ratio of the five-day oxygen utilization value to the 20-day oxygen utilization value decreases as the concentration increases. At an NTA concentration of 2 mg. per liter this ratio is 0.82 and decreases to 0.42 for the NTA concentration of 10 mg. per liter. Under these experimental conditions, the amount of NTA degraded in the BOD determination after five days of incubation is approximately the same regardless of its initial concentration; or as the concentration of NTA increases a small percentage of the total amount of NTA would be degraded in the five days of incubation. Since these ratios vary considerably, a five-day BOD value of this compound would not give any indication of the total concentration of NTA nor a percentage figure for the total BOD of the compound.

These results are similar to those reported by Swisher, Crutchfield, *et al.* (1967), in which they found that NTA was biodegradable in laboratory activated sludge units. They noted that a period of acclimatization was necessary and that removal of NTA was by degradation rather than sorption. They also found that NTA did not affect performance of laboratory activated sludge units.

Summary

NTA can be biologically degraded by organisms in activated sludge following a period of one week for acclimatization of the organisms to this compound. The five-day BOD determination of this compound is zero unless the seed organisms, used in this determination, have been previously acclimatized to this compound. Periods of up to two days without NTA will not adversely effect ability of acclimated organisms to degrade again NTA without time for acclimation.

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Table II. Twenty-Day Oxygen Utilization Requirement of NTA

Concentration of NTA, Mg./L.	Oxygen Utilized in 20 Days, Mg./L. ^a	Oxygen Required, Mg./L. per Mg./L. of NTA	Ratio of 5-Day to 20-Day Oxygen Utilization
2	1.35	0.68	0.82
4	2.45 ^b	0.61 ^b	0.96 ^b
5	3.75	0.72	0.73
8	5.20	0.65	0.49
10	7.10	0.71	0.42

^a Corrected for blank.
^b Based on 15-day value.

Behavior of a Numerical Analog to a Cascade Impactor

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■ A simple numerical analog to cascade impactors and the results of its application to the Andersen sampler are described. Commonly used data reduction techniques overestimate the geometric standard deviation of sampled size distributions. The overestimate is small for geometric standard deviations greater than about 4, but becomes significant for values less than 2. The effects of this artifact on the estimate of median diameter are small. The magnitudes of the errors are related to the shape of the particle size spectrum over the diameter range sampled by the impactor.

The cascade impactor is a device widely used for separating particles according to their aerodynamic diameters. It is easy to operate, rugged, and mechanically simple. Its mechanical simplicity, however, is not matched by the theory covering its behavior. The interpretation of data obtained with cascade impactors involves simplifying approximations of the real behavior to make the problem tractable. Testing the effects of the assumptions through laboratory experiment is a difficult task. This paper presents an alternative to laboratory experiment and discusses some of the results found through application of this alternative to the Andersen sampler (Andersen, 1958).

A cascade-impactor aerosol sampler generally consists of a series of successively smaller orifices or slits through which sampled aerosol passes. The orifices or slits direct the aerosol at a collection surface. The air is forced to make an abrupt change of direction which some particles, because of their inertia, cannot do, and these particles are deposited on the collection surface for subsequent analysis. Because each orifice in the series is smaller than the preceding one, the aerosol is subjected to greater accelerations as it passes successive stages and therefore, at each stage, smaller particles are deposited. Each stage then contains particles within a certain size range.

Ideally a stage would collect all particles larger than a certain size and none smaller; data reduction would be simple and there would be no need for the present discussion. The efficiency of a real impactor stage does not change abruptly from 0 to 100% at some specific diameter, but instead the efficiency varies continuously over a range of diameters. Figure 1 shows the general nature of the collection efficiency of a real impactor stage as a function of particle diameter. The shape of the curve depends on such factors as orifice shape, number of orifices per stage, and spacing from orifice to impaction surface (Ranz and Wong, 1952). Wall losses will also affect impactor behavior, but are not considered here.

One common approach to interpretation of impactor data

approximates the collection efficiency function with the ideal case. The diameter taken to represent the idealized change from 0 to 100% can be chosen in more than one way, but Mercer (1963) has suggested that the diameter at which the stage efficiency is 50% is the best choice.

Figure 1 shows that the real impactor collects some smaller particles which the ideal impactor would not collect, and fails to collect some larger particles which the ideal impactor would collect. If these two quantities, the amounts of uncollected larger particles and collected smaller particles, are equal, then the real impactor stage will capture the same amount of material as the ideal impactor. The diameter at which transition occurs from 0 to 100% efficiency for the ideal impactor can be chosen such that the real and ideal impactors collect the same amounts of material. The diameter which yields this quality is called the effective cutoff diameter of the stage.

Unfortunately, the effective cutoff diameter is a function of the size distribution of the particles which are sampled as well as the parameters of the impactor stage. For example, the effective cutoff diameter can be decreased by increasing the number of smaller particles and decreasing the number of larger particles in the region of the impactor's cutoff. Furthermore, for a given particle distribution, the effective cutoff diameter of a stage varies according to whether the analysis is on a number basis or a mass basis.

The problem of determining a representative cutoff diameter suggests that other data reduction methods should be developed. Mercer (1963) has suggested that the real collection efficiency curves might be approximated with a sloping straight line. A technique based on this approximation (Ludwig, Coulson, *et al.*, 1966) has been proposed, but until now there has been no convenient way of evaluating its performance over a large range of particle size distributions.

In principle, it should be possible to generate and sample aerosols in the laboratory and then to compare the results

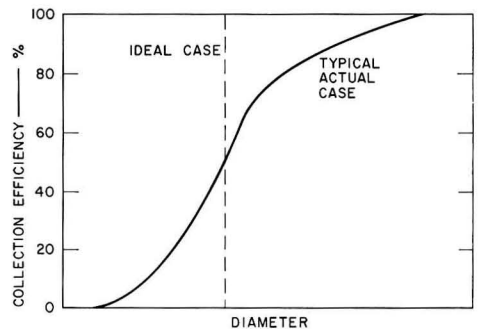


Figure 1. Collection efficiency of an impactor as a function of particle diameter

obtained by various data reduction techniques with the results obtained by some independent sizing method. Anyone who has ever attempted such an experiment will immediately recognize the gap between principle and practice. The difficulties extend far beyond the enormous amount of laboratory work involved, and the chief difficulty is in achieving an accuracy in all the various aspects, such as chemical analyses and particle counts and measurements, so that one can recognize differences in the data reduction techniques. Furthermore, if the sampler is modified, the experiments must be repeated.

An alternative to laboratory experimentation lies in the equations governing the behavior of a cascade impactor. If one assumes that the change of collection efficiency with particle diameter can be specified, it is easy to write equations for the amount of material collected by an impactor stage from a known particle-size distribution. It is not always easy to solve the equations once written, but in principle we can simulate the behavior of the impactor mathematically; this simulation is easier to perform than are laboratory experiments.

Numerical Analog to Cascade Impactor

A general expression for the amount of material, G_m , collected on the m th stage of an impactor is

$$G_m = \int_0^{\infty} E_m(D)F_m(D)dD \quad (1)$$

where $E_m(D)$ is the collection efficiency of the m th stage as a function of aerodynamic particle diameter, D ; and $F_m(D)$ is the size distribution of material entering the m th stage. The expression $F_m(D)$ can be a conventional frequency function, in which case G_m is the total number of particles on stage m , or $F_m(D)$ can be a mass distribution function and then G_m will be the mass of material collected on the m th stage. $F_m(D)$ is the original size distribution modified by the amount collected on the stages preceding m . The expression $E_m(D)$ can be some analytical function approximating the actual collection efficiency function or it can be specified empirically. If $E_m(D)$ and $F_m(D)$ are sufficiently simple functions, Equation 1 can be integrated analytically. Generally, it is necessary to integrate numerically. The set of procedures used to calculate solutions to Equation 1 for each stage constitutes a numerical analog to a cascade impactor.

The computer program which was used to evaluate Equation 1 first calculates and stores values of the size distribution function. Different size distributions, such as normal and log-normal, can be introduced in this first section of the program. Calculations are performed at 0.1-micron intervals from zero microns to the smallest diameter at which the first stage (the stage at which the aerosol enters the sampler) is 100% efficient; this diameter serves as a convenient place to terminate the calculation.

The next step in the calculation is to read the diameters which bound the interval where each stage has a collection efficiency different from 0 or 1. Then, the collection efficiency of the first stage is defined at 0.1-micron intervals. For small diameters this value is 0; for large diameters, it is 1; and for intermediate diameters, the value is read from the experimental data provided. The product of the efficiency and the frequency function is determined; this is the integrand in Equation 1. The value of the frequency function is reduced by

this product to give the value entering the next stage. Determination of a collection efficiency, multiplication of size distribution function by efficiency, and reduction of the frequency function are continued at 0.1-micron diameter intervals through all values within the operating range of the instrument.

After products of frequency function and collection efficiency have been obtained, the integration is performed using Simpson's rule. When the integration has been completed for a given stage the results are printed. The calculations proceed to the next stage, where the collection efficiencies are determined, multiplied by the values of frequency function, and integrated. This continues until calculations have been completed for all stages.

The computer program was written in the programming language BASIC (Kemeny and Kurtz, 1966). The computations were made on a time-sharing system using the facilities of the General Electric Co., Berkeley, Calif.

The model was developed to improve the reliability of particle-size distributions obtained with a particular impactor, the six-stage Andersen sampler (Andersen, 1958). Application of the numerical analog to this instrument will illustrate some of the general characteristics of cascade impactor behavior.

To simulate the Andersen sampler numerically, the collection efficiency of each stage as a function of diameter must be known. Figure 2 shows the empirical curves used. The empirical curve for stage 1 comes from the work of Ranz and Wong (1952), using the values for the physical stage parameters given by Andersen (1958). Stages 2 and 3 are based on the work of Flesch, Norris, *et al.* (1967), who used electron microscopy to size methylene blue aerosols. The last three stages use Flesch's curves determined with an electron microscope and monodisperse polystyrene latex aerosols. The curves have been extrapolated to the 0 and 100% collection efficiencies. For purposes of calculation, a completely efficient filter was used as the seventh stage.

The numerical analog was used to sample size distributions of the form:

$$F_1(D) = \frac{100}{D\sqrt{2\pi} \ln \sigma_g} \exp \left\{ - \left[\frac{\ln(D/\bar{D}_g)}{\sqrt{2 \ln \sigma_g}} \right]^2 \right\} \quad (2)$$

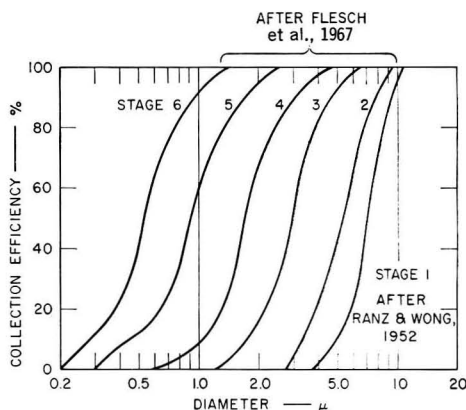


Figure 2. Andersen sampler collection efficiencies

This is a log-normal distribution (on any desired basis—e.g., mass or number) with geometric standard deviation, σ_g , and geometric mean, \bar{D}_g . The units of $F_1(D)$ are per cent per micron (of diameter interval) when D and \bar{D}_g are expressed in microns. The value of Equation 2 integrated from 0 to 10.6 microns (the point at which stage 1 is 100% efficient, Figure 2) can be determined from tables and the answers compared with the total amounts of material collected by all stages of the numerical impactor. The two answers should be the same, and any differences result from inaccuracies in the numerical integration process used in the model. In all cases presented here, the values differed at most by $\pm 0.3\%$, and agreement was usually much better than that. However, because of large truncation errors (differences between the analytical and the numerical integrations) the model is unsuitable for cases with large values of σ_g and small values of \bar{D}_g . It could undoubtedly be improved by the use of smaller intervals of D in the integration process.

The model is not restricted to sampling log-normal size distributions, and in fact it has been used with good results on distributions having the form of Legendre polynomials. Almost any size distribution which can be specified analytically can be sampled.

Results

The numerical analog was used to simulate cascade-impactor sampling of several log-normal size distributions with median diameters from 1 to 8 microns and geometric standard deviations from 1.5 to 4. The results of these simulations are shown in Figure 3, plotted on log-probability graphs. Figure 3 also shows the results obtained by hand calculation using Equation 1 for monodisperse aerosols ($\sigma_g = 1$). The heavy lines represent the sampled size distributions in which the integral of $F_1(D)$, from zero to D , is plotted against $\log D$. The probability scale used for the abscissa is such that log-normal distributions will plot as straight lines.

If an Andersen sampler had been used and had collected the amounts on each stage indicated by the numerical analog and if these cumulative collections had been plotted against the 50% efficiency diameters (D_{50}) for the appropriate stages, then the points shown in Figure 3 would have resulted.

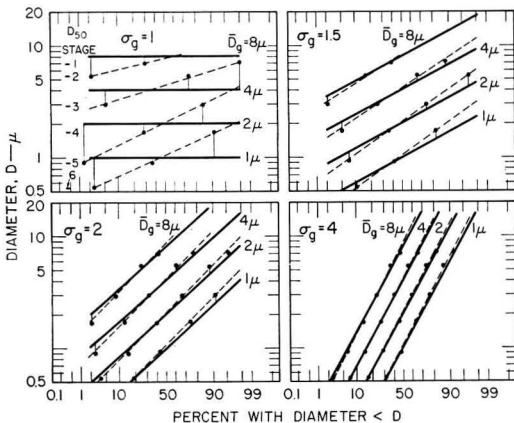


Figure 3. Calculated results of sampling a variety of size distributions with the Andersen sampler

This is probably the most common method of data reduction. In the figure, the points corresponding to the 50% efficiency cutoff assumption have been connected to the sampled size distributions with vertical lines (lines of constant cumulative percentage). These vertical lines and the size distribution cross at the "true" effective cutoff diameter for that stage and for that size distribution. If this "true" value is used, a point on the sampled size distribution is exactly specified. This is not always true of the D_{50} assumption.

Often the points specified by the impactor stage collections and by assumption of effective cutoffs at the D_{50} diameters are plotted on log-probability graph paper and then fitted with a straight line to specify the best fitting log-normal distribution for the data. The dashed straight lines, which were visually fitted to the plotted points of Figure 3, are invariably steeper than the lines representing the corresponding sampled distributions—that is, the D_{50} cutoff assumption yields values of geometric standard deviation which are too high. The monodisperse aerosol ($\sigma_g = 1$) represents a limiting case. This is the smallest possible standard deviation. Figure 3 shows that it results in the largest error of the estimate for the true geometric standard deviation. As the actual standard deviation increases, the estimates made using D_{50} cutoff values tend to become better. The results shown for the monodisperse case indicate that impactor collections would yield a value of σ_g equal to about 1.5 at a minimum when calculated on the basis of the D_{50} cutoff assumption.

Figure 3 illustrates several things. It can be used to define the true values of effective cutoff diameter for each stage and for the different combinations of median and geometric standard deviation. This figure also illustrates the consistent overestimation of σ_g which results from common data reduction techniques. Finally, it shows that the D_{50} cutoff assumption leads to reasonably accurate estimates of median diameter. There is a slight bias toward overestimation, however.

An earlier section implied that the effective cutoff diameter of an impactor depended on the slope of the frequency distribution curve, $dF_1(D)/dD$, for values of D near the cutoff diameter. When the slope is increased, the effective cutoff diameter should also increase. Figure 4 shows this relationship. The slope of the size frequency curve was calculated for each of the twelve heterodisperse size distributions shown in Figure 3 at each of the six D_{50} 's corresponding to the six stages of the Andersen sampler. The expression for the slope of the size distribution curve is:

$$\frac{dF_1(D)}{dD} = - \frac{100}{D^2 \sqrt{2\pi \ln \sigma_g}} \exp \left\{ - \left[\frac{\ln(D/\bar{D}_g)}{\sqrt{2 \ln \sigma_g}} \right]^2 \right\} \times \left[\frac{\ln(D/\bar{D}_g)}{\ln^2 \sigma_g} + 1 \right] \quad (3)$$

The corresponding effective cutoff diameters were determined from Figure 3 for the heterodisperse aerosols. The collection efficiency curves of Figure 2 were consulted to determine the collection efficiency at the effective cutoff diameter. These collection efficiencies were plotted against slope, $dF_1(D)/dD$, determined from Equation 3. The slope is not necessarily applicable to the size distribution entering any stage but the first. A separate graph was prepared for each stage. Only those data were used where the cumulative

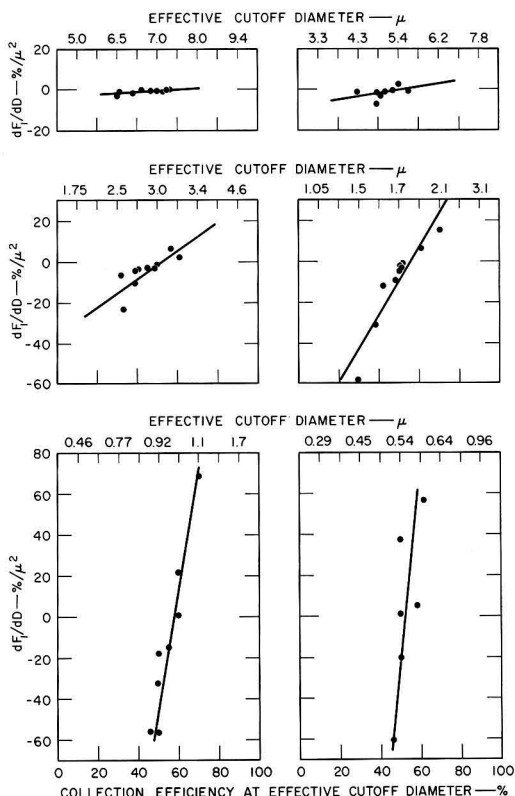


Figure 4. Dependence of effective cutoff on slope of the size frequency distribution

percentages in Figure 3 were between 5 and 95%. Outside this range, the determination of effective cutoff diameter was too sensitive to small calculation errors. The lines shown in Figure 4 were visually fitted to the points.

The effective cutoff diameter of stage 1 is very sensitive to the slope of the sampled size distributions (Figure 4); a small change in slope results in a large change in effective cutoff diameter. The opposite is true of stage 6. The changes between form an orderly progression through the intermediate stages.

Figure 4 seems to indicate that the diameter of about 55% collection efficiency might be a better approximation to the effective cutoff diameter than D_{50} . Most of the lines of Figure 4 cross the line of zero slope at about 55% collection efficiency. However, because of the skewness of log-normal distributions, their slope is negative over a much wider range of diameters than it is positive (technically, an infinitely wider range). For this reason, a choice of effective cutoff diameter appropriate to a slope somewhat less than zero might be best; D_{50} is generally appropriate to a slightly negative slope and seems to be a good all-purpose choice.

The scatter of the points in Figure 4 is probably the result of several factors. The factor which seems most important is the overlapping of the diameter intervals over which the various stages collect particles. Except for the first stage, each stage does not collect from a sample which has a log-

normal form, even in the diameter interval covered by the collection efficiency curve of that stage. The first stage does not just truncate the size distribution, but significantly alters it in the region which affects the second stage, and the second stage does the same for the third, etc. Thus the slope of the original size distribution is not necessarily the slope of the size distribution which reaches any given stage. Other factors which probably contribute to the scatter include the shape of the size distribution curve (curvature, rate of change of curvature, etc.) and the associated truncation errors.

Conclusions

These studies show that the numerical analog is a useful tool for investigating the behavior of impactor-type aerosol samplers. The graphs relating effective cutoff diameters to the slope of the size frequency distribution (Figure 4) could probably be used as the basis for an iterative method to improve size distribution estimates based on Andersen sampler data. This has not yet been pursued but, briefly, the technique would involve an initial size distribution estimate based on D_{50} values for the stages. The slope of this estimate would be used to determine a new set of effective cutoff diameters from the curves of Figure 4. The cutoff diameter estimates would, in turn, yield a new size distribution estimate. The iteration would continue until the estimates converged.

The studies with the numerical model have also indicated areas where it could be improved. The possible improvements appear to lie mostly in the realm of the numerical methods used to integrate the equation. The specification of collection efficiencies at smaller intervals of diameter, with concomitant use of smaller diameter intervals in the numerical integration, should lead to better results. However, such changes would be accompanied by increased computation time and data storage requirements. Analytical functions could be used to approximate the experimentally determined collection efficiency curves. Use of such functions and smaller diameter intervals for the numerical integration should provide greater accuracy in some cases without increasing data storage requirements.

Acknowledgment

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Concentration and Ultrasensitive Chromatographic Determination of Sulfur Hexafluoride for Application to Meteorological Tracing

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■ Dilutions of sulfur hexafluoride in air can be determined down to a sensitivity of 1 part of SF₆ in 10¹⁴ parts of air. Samples are concentrated by an adsorption-desorption process using an activated charcoal trap. The desorbed SF₆ is determined by means of a gas chromatographic procedure using an electron capture detector. The ultrasensitivity of the method requires that the carrier and sample diluent gases be free of SF₆ and other electron-absorbing impurities. Precautions and methods of avoiding spurious peaks are described. Sample collection and the preparation of calibration mixtures in Saran bags are discussed. Consideration is given to the accuracy of the results as well as typical performance characteristics. Efficiency drops as sample size is increased. Recoveries in excess of 80% are reported for 250-ml. samples. The determination of the distribution of concentrations of SF₆ taken downwind from a release point demonstrates meteorological application over a range of 75 miles. Data were obtained on the atmospheric concentration of SF₆ in residential and urban areas. This analytical technique offers a fast and reliable way to study the transport of pollutants by monitoring the dispersion of an inert gaseous tracer.

The use of sulfur hexafluoride in meteorological tracer studies has been described in several recent papers (Collins *et al.*, 1965; Niemeyer and McCormick, 1967; Saltzman *et al.*, 1966; Turk *et al.*, 1965, 1968). Sulfur hexafluoride can be determined to very dilute levels by means of gas-solid chromatography with electron capture detection (Clemons and Altschuler, 1966). Direct determination with a sensitivity of 10 picoliters per liter has been reported (Saltzman *et al.*, 1966). This sensitive method coupled with the inertness of SF₆ showed considerable potential for pollutant-transport studies, but greater sensitivity was needed for long distances. Even if the tracer were released under very good conditions, a slight change in wind direction would change the anticipated local concentration of SF₆ by a thousandfold or more. A method applicable over a range of concentrations from 0.01 picoliter per liter to several parts per million was needed.

A number of concentration procedures have been described (Bellar *et al.*, 1963; Brenner and Etre, 1959; Cropper and Kaminsky, 1963; Neligan *et al.*, 1965; Novak *et al.*, 1965; Widmark and Widmark, 1967). Each offers a novel way to condense, concentrate, and determine one or more dilute contaminants in air, but none has been demonstrated at a sufficiently high level of sensitivity or applied to SF₆. However,

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Turk *et al.* (1968) successfully concentrated SF₆ using liquid oxygen as a coolant, reporting that the one part per billion sensitivity could be enhanced at least 2000-fold by freeze-out concentration. The use of activated charcoal to adsorb and concentrate traces of SF₆ in air with subsequent release of the sample for gas chromatographic analysis is described in this paper. Consideration is given to accuracy and efficiency as well as to typical performance characteristics. The procedure establishes a new level of analytical sensitivity (one part in 10¹⁴ by volume) and opens a broad area of application to ultrasensitive analysis previously unattained.

Experimental

Gas Chromatographic Systems. Any gas chromatograph equipped with an electron capture detector could be adapted for use in the manner described. The equipment used in this study was basically a MicroTek 2500 Series gas chromatograph, equipped with a Barber-Colman Model 5120 adjustable anode electron capture detector, a Keithley Model 417 Picoammeter, a MicroTek polarizing voltage power supply providing 0 to 50 volts d.c., and a Minneapolis-Honeywell Series 153 1-mv. recorder. The column, in two sections, consisted of 15 feet of 1/8-inch-o.d. stainless steel tubing packed with 40-60 mesh Baymal (Kirkland, 1963). The first 3 feet of the column was used as a cutter column and the remaining 12 feet as an analytical column. The system was optimized as previously reported (Saltzman *et al.*, 1966). The column and detector were operated at ambient temperature. The carrier gas was 5% hydrogen in argon, flowing at 75 ml. per minute; the electron capture detector contained a 500-mc. tritium foil and was operated at 20 to 25 volts with an electrode spacing of 1.5 cm. This produced a current of 12 nanoamperes. Two MicroTek gas sample valves, one seven-port and the other nine-port, were used to mount the charcoal trap injection system and a cutter column with backflush connections, respectively. Several features were added to the system to permit the analysis of extremely dilute sample concentrations. Carrier gas purification and cutter column backflushing arrangements were included to remove the many unwanted materials that were also concentrated.

A schematic flow diagram is given in Figure 1. The carrier gas passed through two 165-gram canisters of BTS catalyst, a reduced form of CuO used for the removal of oxygen (Maak and Sellars, 1965), then through two 165-gram canisters of 5A molecular sieve. The carrier gas stream was then split. The side stream passed to sample valve 13, providing backflushing gas for the cutter column. The main stream passed through various flow control devices. Both streams were further purified by charcoal filters 7; these were regenerated every 72 hours by heating in the manner described below for the sampling trap. Next, the main carrier gas stream flowed to gas sample valve 8, and passed through carbon trap 9 or

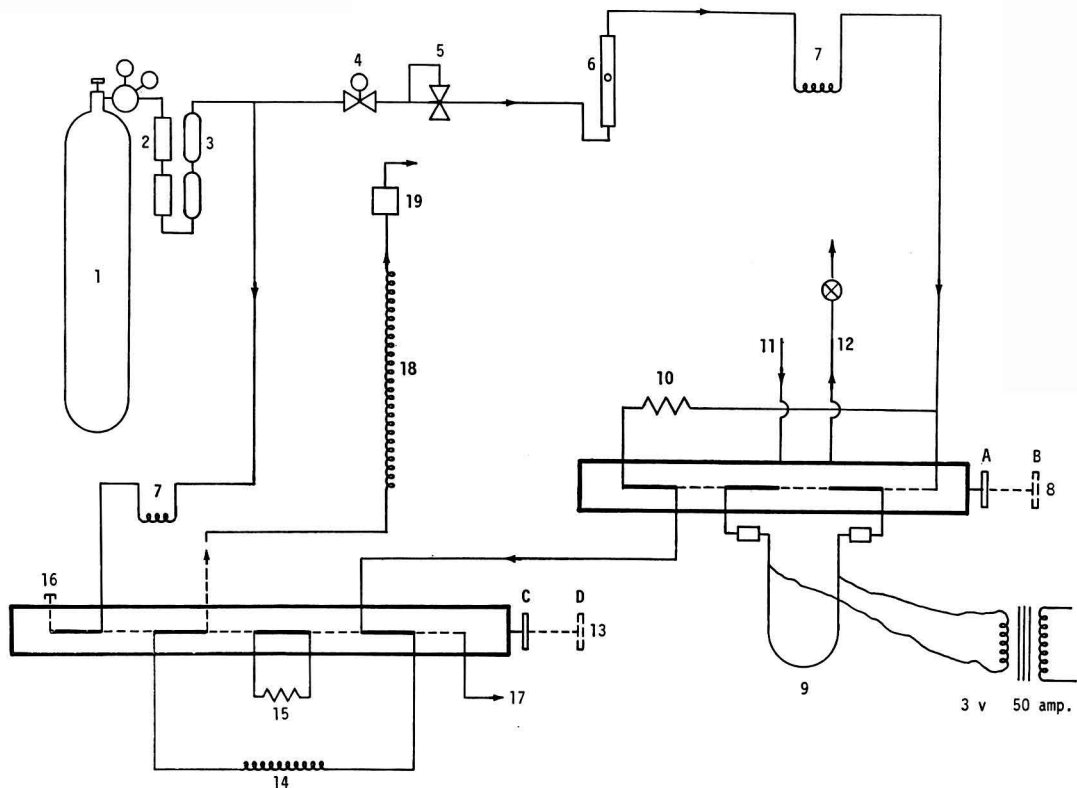


Figure 1. Flow schematic of inlet and trapping system

- | | | |
|---|--|--|
| 1. Carrier gas | 8. Seven-port valve | 14. Cutter column |
| 2. Canisters of BTS catalyst | 9. Sample trap with heater | 15. Flow resistance matched to cutter column |
| 3. Canisters of molecular sieve 5A | 10. Matched flow resistance | 16. Capped port |
| 4,5. Flow controls | 11. Sample entry | 17. Exit for backflush |
| 6. Flowmeter | 12. Exit to vacuum source through needle valve control | 18. Analytical column |
| 7,7. Charcoal traps for purification of carrier | 13. Nine-port valve | 19. Detector |

through a matched flow resistance 10, and thence to gas sample valve 13. There the carrier gas had two possible paths: through the 3-foot cutter column of Baymal 14 (valve position C) or through a flow resistance 15 matching that of the cutter column while the latter was being backflushed (valve position D). Finally, the carrier passed through the analytical column and to the detector. The flow resistances of the system were balanced carefully so that operation of the sample valves did not change the flow rate through the detector and thus alter the current.

Concentration System. Typically, the adsorbent tube ($1/8$ -inch-o.d. stainless steel) was packed with 1 gram of charcoal, coiled, and connected in place of the existing gas sample loop on the gas sample valve. A 1-kv.-amp. 12-volt filament transformer, supplied with power through an adjustable autotransformer, was used to heat the carbon-packed tube; a heavy current was passed directly through the length of tubing so that the sample was desorbed rapidly enough to give a sharp peak in the detector. The electrical connection was made directly to the tubing rather than to a fitting. The tubing was electrically insulated from the valve with Teflon tubing. The trap was conditioned for use by passing

current from the filament transformer through the stainless steel tube for about 15 minutes while flushing with clean inert gas. The current was adjusted to provide a surface temperature of about 500° C. as indicated by the dull red color of the tube. Once the adsorbent tube was conditioned, it was connected to the valve and could be used repeatedly.

Analytical Procedure. Samples were collected in Saran bags as previously described (Saltzman *et al.*, 1966). The basic analytical procedure was as follows: The bag containing the sample or standard mixture is connected to port 11 and a suction is applied to port 12 on gas sample valve 8 (Figure 1). A needle valve in the suction line ensures a uniform rate of flow (30 ml. per minute) and can be disconnected when a sample under pressure is taken from a cylinder. Once the desired volume of sample has passed through the carbon, about 20 ml. of nitrogen free of SF₆ is drawn through the system to remove large quantities of oxygen that may be collected in the interstices of the packing so as to prevent injection of the oxygen into the chromatographic system.

For injection of the sample, the setting of the gas sample valve is moved from A to B, so that the carrier gas passes through the trap in the reverse direction. The sample is de-

sorbed from the carbon by passing current from the transformer for 10 seconds through the stainless steel tubing of the carbon trap, which is used as a resistance heating element. The voltage is preselected to heat the tube to a dull red in the time applied. The stem of the gas sample valve is kept in position *B* for 20 seconds to allow time for elution of the sample from the trap into the cutter column essentially as a slug; then the valve stem is returned to position *A*. After a total elapsed time of 1 minute, valve 13 is moved to position *D* to backflush and vent the slower-moving components of the sample. The total retention time for SF₆ is 3 minutes; it passes through the cutter section in 0.6 minute. The analysis is complete in about 5 minutes. After the SF₆ is eluted from the system, valve 13 is returned to position *C* and the carbon trap is cooled to 25° C. with cold water before the next sample is adsorbed. A uniform volume is taken for analysis from field samples so that the concentrations of SF₆ in each sample can be read directly from a calibration curve. In this way, all the empirical factors of the method are incorporated into the calibration curve.

Calibration. Saran bags were used to prepare and store the dilute concentrations of SF₆. Calibration curves covering the range from 0.01 to 2.5 p.p.b. were prepared by the direct injection of samples using a 0.5-ml. loop in place of the carbon trap. Further dilution was required to obtain working standards in the picoliter per liter range. Multistep dilution (Saltzman *et al.*, 1966), and a flow dilution apparatus (Saltzman and Clemons, 1966), were successfully used to prepare dilute concentrations. The validity of these dilution techniques was proved by the logarithmic dilution procedure (Lovell, 1958). Semilogarithmic plots of detector responses showed a linear relationship over a range of three decades of peak height. The linearity of the plots (for the three-component mixture) was evidence of the validity of the calibrations at the lower limits of measurable concentrations. These plots were used to check the accuracy of standards prepared by various dilution techniques.

Permeation tubes (O'Keeffe and Ortman, 1967) may eventually provide standard concentrations of SF₆ in the picoliter per liter range. The major advantage claimed for the permeation tube is that precise amounts of SF₆ would be continuously available for a year or more. Standard concentrations of SF₆ prepared by current dilution techniques are useful for only a few days.

Results

Screening of Adsorbents. Several potential adsorbents including alumina, silica gel, molecular sieves, and activated carbons were evaluated for both retention and release properties. Many types of activated carbon were tested; Darco activated charcoal (a lignite charcoal), Burrell activated charcoal (a coconut charcoal), and a Barnebey Cheney coconut charcoal (designated GI) received the most study. Measured amounts of these adsorbents in 1/8-inch-o.d. tubes were placed in the sample line of the chromatograph. Known volumes of air sample containing SF₆ were passed through the tubes and sampled periodically to determine the exiting SF₆ concentrations. Typical retention values for a 0.5-p.p.b. SF₆ mixture are shown in Table I. All work reported here was conducted at room temperature.

Because activated charcoal clearly showed the most promise as an adsorbent for SF₆, traps packed with this material were studied in detail.

Table I. Retention of SF₆ by Adsorbents

Adsorbent	Retention Volume, ^a ML./G.	Retention Mass, ^b Nanograms/G.
Al ₂ O ₃ (Alcoa F-10)	88	0.2
Silica gel (Burrell, 300° activation) (50-60 mesh)	333	1.0
Silica gel (Burrell, 450° activation) (50-60 mesh)	667	2.0
Molecular sieve (13X)	833	2.5
Coconut charcoal, (50-60 mesh) (Burrell)	3200	9.5

^a Adjusted to value for 1 gram of adsorbent packed in 1/8-inch-o.d. stainless steel tubes.

^b Adjusted to value for sample containing 0.5 p.p.b. SF₆.

Typical Calibrations. No noticeable adsorption of SF₆ by the Saran bags at these low concentrations was observed. Field samples as well as prepared concentrations were stored for periods up to 2 weeks without measurable losses. The data presented below were obtained with mixtures prepared by dilution of known concentrations, which were established with the aid of freshly prepared calibration curves.

A major consideration in the preparation of dilute concentrations of SF₆ was to ensure that the diluent gas was free of SF₆. Zero-grade air sometimes was found to contain as much as 0.6 picoliter per liter of SF₆, and many cylinders of hydrogen in argon and of prepurified nitrogen contained as much as 0.4 p.p.b. of SF₆. Analysis of each cylinder before use was necessary to ensure rejection of impure gas.

Figure 2 shows some results obtained with several concentrations of SF₆. Multiple volumes were drawn through a trap 0.105 inch in i.d. and 20 inches long containing 1 gram of charcoal. Sample volumes as large as 400 ml. were concentrated with recoveries of more than 60%. Further examination of Figure 2 shows that the relationship between concentration and peak height at a given volume was approximately linear. Figure 3 shows the effects of different tube dimensions. As would be expected, sample capacity increased with tube size. These data were obtained with 20-30-mesh Darco charcoal. Reproducibility for successive volumes of the same sample concentration is indicated in the chromatograms of Figure 4. No significant difference in peak height is apparent for the four replicate 200-ml. samples. A calibration curve similar to that shown in Figure 3 was obtained when a single sample size was used to obtain the data points.

Over-All Recovery. The column and detector system was calibrated with standard concentrations of SF₆ by direct injection using a 0.5-ml. gas sample loop, with results shown in Figure 5. Accurate dilutions of these standards were prepared in Saran bags; various volumes were drawn through the trap and analyzed by the recommended procedure. The peak heights were converted to picoliters of sulfur hexafluoride by use of the calibration curve. The ratios of these quantities to those calculated to have entered the trap were taken as the recoveries. The calculated quantity was the sample volume divided by the dilution factor, multiplied by the known concentration of the undiluted standard.

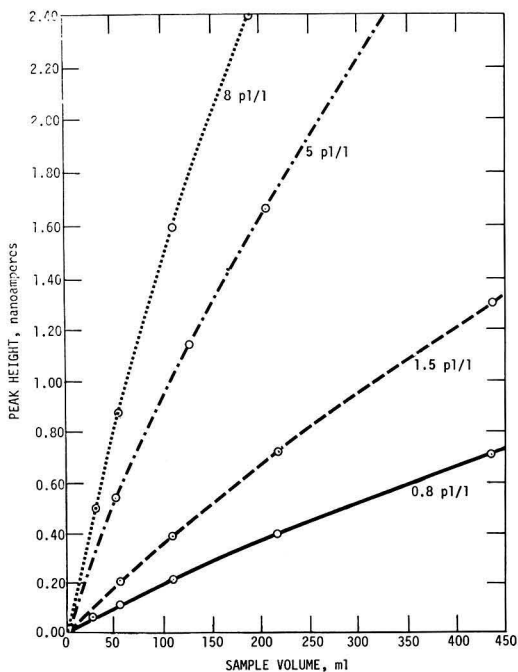


Figure 2. Effect of concentration and sample volume of SF₆ on peak height

Adsorbent, 1 gram of Darco granular charcoal, 20-30 mesh

Table II shows that recoveries of 80% or greater were obtained for sample volumes as large as 200 ml. and sample concentrations up to 2.5 picoliters per liter. These results suggest that samples up to 1 liter could be concentrated on higher-capacity carbons. This procedure would permit the determination of SF₆ concentrations as low as 10^{-15} volume per volume.

Efficiency dropped as sample concentration and the volume of sample taken increased. At the higher concentrations the

Table II. Effect of Concentration and Size of Sample on Recovery from Darco Charcoal (Per cent recovery)

Sample Concn., Pl./l.	Volume, MI.					
	28	55	110	220	440	590
0.8	94	92	87	80	73	68
1.5		89	83	81	72	71
2.5	94	92	83	76	68	
5	76	75	64	63		
8	80	71	69	67		

breakthrough of SF₆ from carbon was gradual. At the low concentrations used, the breakthrough was difficult to detect. It may well be that not all the sample gas in contact with the charcoal was retained. The data for efficiency suggest that such losses increased as the amount of SF₆ to be trapped was increased.

The shape of the SF₆ peak after desorption was similar to that of one of the same size obtained from a direct analysis from a 0.5-ml. gas sample loop. Since the widths at half peak and the areas are the same, the peak heights for the same amount of gas should be the same. It is likely, therefore, that the losses in peak heights represent losses of SF₆ in the trapping procedure rather than artifacts.

Discussion

Physical Factors in Trapping Method. The maximum permissible sample volume for quantitative retention of a compound in an adsorption tube can be related to the breakthrough volume, determined by carrying out a frontal analysis in which a mixture containing the compound is passed at a constant flow rate through the tube connected in turn to a detector. The retention volume concept explains the behavior of SF₆ passing through a carbon-packed tube. The carbon trap can be regarded as a chromatographic column; the first trace of SF₆ will elute from the trap at the same time regardless of the gas concentration. In this system the samples were pulled through the trap under vacuum. The trapping efficiency was reduced when higher vacuum was required. The better

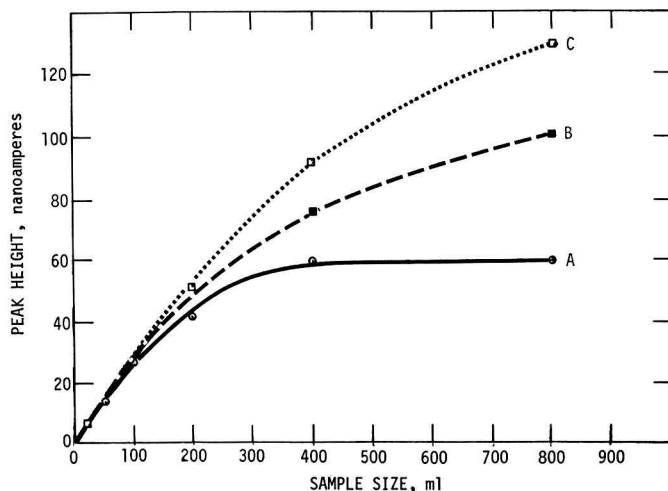


Figure 3. Effect of quantity of adsorbent on sample volume and peak height

A. 0.105 inch i.d. × 7.5 inches, 0.5 gram of charcoal
 B. 0.21 inch i.d. × 7.5 inches 1.8 grams of charcoal
 C. 0.21 inch i.d. × 28 inches, 6.6 grams of charcoal

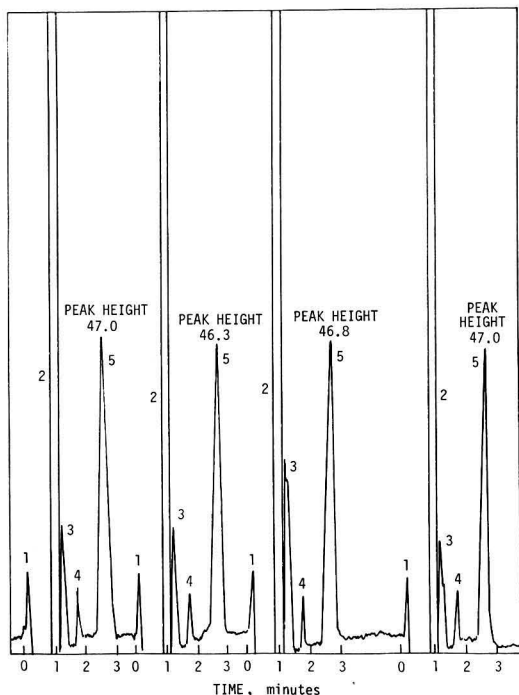


Figure 4. Reproducibility of successive 200-ml. sample injections

- 1.4. Flow artifact
- 2.3. Air peak
- 5. Sulfur hexafluoride

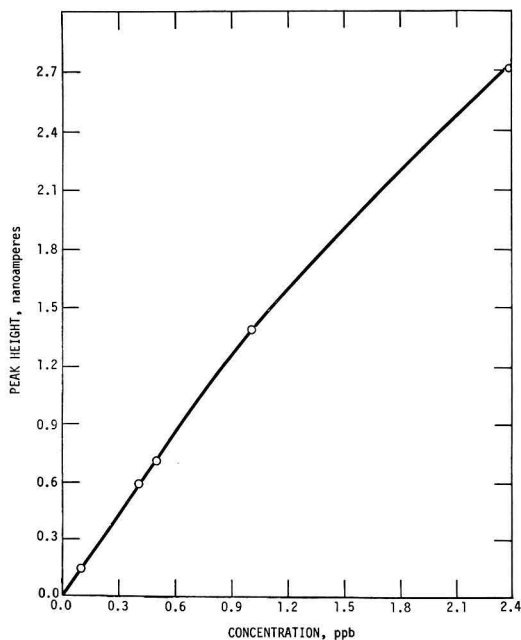


Figure 5. Calibration curve for SF₆ by direct determination
0.5-ml. sample loop

traps were those having low flow resistance—for example, 20–30-mesh charcoal was more efficient as a trap packing than 50–60-mesh charcoal because less vacuum was required for a given flow. The capacity of a given trap depended upon the quantity of charcoal in the trap; however, a large quantity of charcoal was not required.

Interfering Peaks. To avoid spurious peaks and other undesirable effects, each step in the procedure should be performed exactly as outlined. For ultrasensitivity, even the best available carrier gas must be further purified. The elaborate cleanup procedure specified has proved to be necessary. Failure to regenerate the traps when required resulted in loss of sensitivity and general degradation of the base line with peak after peak from unwanted materials continually eluting from the system. From atmospheric samples as well as those prepared with prepurified nitrogen, enough unwanted material was concentrated that omitting one of the steps in the analysis deprived the operator of the use of the instrument for several hours.

Background Levels of SF₆. Background levels of SF₆ were estimated from production and consumption data provided by manufacturers and users of SF₆. Because of its chemical inertness, the total quantity of SF₆ that was calculated to have escaped was assumed to be uniformly distributed in the global atmosphere without loss. The calculation indicated that the concentration of SF₆ could be expected to rise to as high as 1 picoliter per liter in the vicinity of SF₆-manufacturing plants and world-wide should be at least 10⁻⁴ picoliter per liter.

An atmospheric sample as small as 250 ml. was sufficient to detect background levels of SF₆. In a number of samples taken in and around Cincinnati, Ohio, in urban and in residential areas, values ranged from 0.04 to 0.20 picoliter per liter. No sample was found to be free of SF₆. When applied to samples of carefully selected nitrogen, the procedure shows no detectable blank.

Tracer Applications. The concentration of SF₆ with activated carbon has been used extensively in a number of meteorological tracer tests. For example, air movements were tracked over distances of 75 miles with SF₆ as the tracer by release of about 1 pound per minute of the gas from cylinders for 1 hour. Sampling arcs were laid out downwind at distances of approximately 20, 40, and 75 miles; eight to ten samplers were located at 2-degree intervals on each arc. Last-minute adjustments were made in the sampler locations to center them about the midpoint of the tracer mass, by observing the probable path of the tracer mass with the aid of tetroons (tetrahedron-shaped constant-volume balloons) which were released at several times prior to the test. Sampling was started 15 minutes prior to the estimated time of arrival and stopped 15 minutes after its estimated passing. At each site, air samples were pumped into Saran bags, which were brought to the laboratory and later analyzed for SF₆. Typical values for a series of sequential grab samples taken at the beginning of 15-minute intervals are shown in Figure 6. The SF₆ cloud is easily determined to be of 1 hour's duration by the rise and fall of SF₆ concentrations. The tracer in this run had been released during the time 0900 to 1000 hours at a point 72 miles upwind.

The Saran bags were adequate for collection of samples, provided precautions were observed in their use. The low but finite permeation rate of Saran (about one half that of

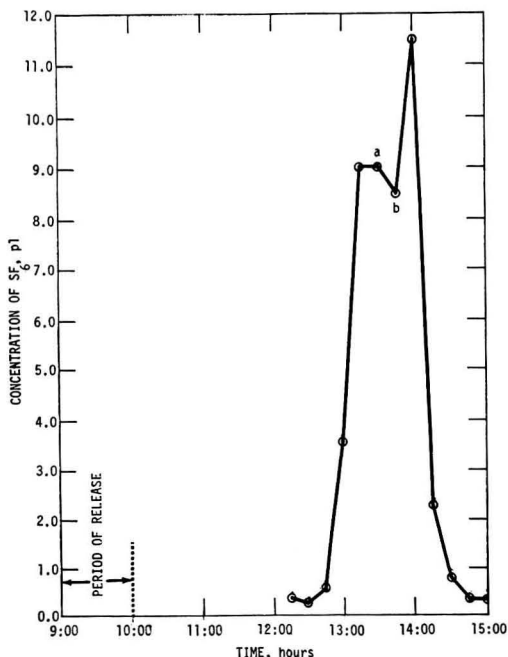


Figure 6. Concentrations found in sequential samples from field test
Small leaks found in bags containing samples a and b

Mylar) made it useful for the storage of samples and standards. These mixtures were kept in bags for at least 2 weeks without perceptible change. Bags of sample that are low in SF₆, however, should not be exposed in locations at which the concentration of the tracer is much higher. As a result of net inboard permeation, unusually high concentrations of SF₆ will accumulate in the bag. At one time in the experience of this laboratory, background samples collected before the start of a field test were kept for the test's duration in a truck about 15 feet upwind from the site of release of SF₆. Subsequent analysis of the contents of these bags showed contamination with abnormally high concentrations of SF₆. Bags made of Saran must be carefully inspected for leaks before use. This is particularly important for bags with a history of use, since repeated folding and manipulation of the bag increase the probability that small cracks or holes will develop.

Traces of SF₆ from previous use must be removed from sampling containers, by purging two or three times with nitrogen (or another clean gas to which the electron capture detector does not respond). Air is not recommended for this purpose because it is usually compressed directly from the atmosphere and, if so derived, will contain background concentrations of SF₆.

Another potential use for this concentration procedure is the tracking of stack effluents. Transport of pollutants from a single stack in the midst of others could be determined by injecting tracer gas into it. The data obtained would offer a firm quantitative basis for ascertaining the importance of individual sources of pollution. This technique can also be used to determine the relative degree of ground-level pollution

from substances emanating from high and low stacks.

It is possible that the background level of SF₆ will gradually increase until eventually another tracer gas will be needed. Halogenated compounds with a sensitivity of detection equal to that of SF₆ are available (Clemons and Altshuller, 1966). Gases with special characteristics may be needed to meet special tracer requirements for future applications.

Conclusions

Atmospheric samples can be analyzed for sulfur hexafluoride at an extraordinary level of sensitivity heretofore not reported for routine use. The sampling and analytical procedures for concentrations of SF₆ down to atmospheric background levels are convenient and rapid. This technique opens an area of research on other pollutants that exist at very dilute concentrations in the atmosphere but have not been studied because a sufficiently sensitive analytical method was not available. The optimal tube size that would allow the successful concentration and analysis of samples up to 1-liter volume is still under study. The procedure as it now stands can, without major modification, successfully employ tubes containing several grams of activated charcoal. Recoveries of over 80% are obtained and, if the precautions are observed, the technique is fast, accurate, and reliable for determining the attenuation of SF₆ concentrations over a distance of a hundred miles.

Acknowledgment

Appreciation is expressed to A. E. O'Keeffe for valuable discussions concerning the interpretation of the work, and for his contributions in obtaining some of the background information in this paper.

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COMMUNICATION

Glycolic Acid in Natural Waters and Laboratory Cultures

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■ The presence of glycolic acid in Madison, Wisconsin, lakes has been studied over a two-year period. An ion exchange concentration procedure enabling the detection of 40 μg . of glycolate failed to establish any evidence for the presence of glycolate in these lakes. It was concluded that glycolic acid is not present universally in natural waters in detectable concentrations. Laboratory studies have shown that certain strains of *Chlorella pyrenoidosa* do accumulate glycolic acid in the culture medium.

The importance of extracellular products of phytoplankton to the ecological balance of natural waters has become the subject of increasing concern over the past decade. Although these excretory products may represent only a minor fraction of the total dissolved organic matter in natural water, their impact and over-all effect is thought to be of major importance. One compound which has received much attention in recent years is glycolic acid. The accumulation of this compound in substantial quantities (3 to 8 mg. per liter) in the supernatant liquid of actively photosynthesizing cultures of *Chlorella pyrenoidosa* was first reported by Tolbert and Zill (1956) and has been substantiated by several other studies (Nalewajko, Chowdhuri *et al.*, 1963; Pritchard, Griffin *et al.*, 1962; Spear, 1966; Warburg and Krippahl, 1960). The possibility of glycolate accumulation in natural waters in the same range of concentration as in the culture studies has been reported by Fogg and Nalewajko (1963) in their investigation on the waters of the English Lake District. They have proposed, on the basis of their laboratory and field data, that glycolate concentrations may be a limiting factor in the initiation of an algal bloom—i.e., until the surrounding lake waters attain a certain minimal glycolate concentration, exponential growth of the algae cannot proceed. Owing to the implied ubiquity of glycolate in natural waters and its role in the limitation of algal bloom conditions, an investigation into its occurrence in the Madison lakes of Wisconsin (Mendota, Monona, Waubesa, Kegonsa, and Wingra) was conducted. This communication presents a summary of the results of this investigation.

Experimental

Sample Collection. Samples for natural water analyses were obtained by grab sampling of surface waters from the Madison lakes. After collection, the samples were either filtered immediately or within several hours via a 0.45-micron membrane filter. Care was taken during filtration to prevent ex-

cessive clogging of the filters, thereby reducing the possibility of cell rupture with subsequent release of cellular glycolate to the surrounding medium.

Analytical. Calkins' (1943) colorimetric method for the estimation of glycolate was used throughout the investigation. Absorbance readings were made with a Perkin-Elmer 202 spectrophotometer at 530 $m\mu$. Standard glycolate solutions were made from Eastman "white label" calcium glycolate and the color reagent from Eastman "yellow label" 2,7-dihydroxynaphthalene. All other reagents used in this study were made from reagent grade chemicals.

Procedure. During the initial period of the study, 0.2-ml. aliquots of lake water were analyzed directly for the presence of glycolate. Several glycolate concentration techniques, including steam and vacuum distillation, as well as heat and ion exchange concentration of water samples, were employed when the direct analyses failed to indicate the presence of detectable amounts of glycolic acid. Steam and vacuum distillation techniques for the concentration of glycolic acid proved unsuccessful. Heat concentration of water samples employed originally was discontinued owing to interference caused by other components present in the concentrated water. An anion exchange gradient elution chromatography technique (Palmer, 1955; Spear, 1966) succeeded in concentrating the glycolate free of interferences.

Results

Field Studies. Studies on glycolate occurrence in natural waters were conducted on the Madison lakes with particular emphasis on the waters of Lake Mendota. Analyses of lake water for glycolate content were initiated in June 1963, and extended throughout the summers of 1963 and 1964. Samples were taken of surface waters at approximately weekly intervals. The direct analysis test for glycolate using the Calkins colorimetric procedure gave negative results for all samples tested. Similar results were recorded for water samples which were concentrated 2- to 50-fold by either evaporation (heat concentration) or anion exchange chromatography.

Ion exchange recovery studies using both 40 μg . and 200 μg . of added glycolate per liter of Lake Mendota water proved successful. The latter recovery was better than 90% in an eluate volume of 18 ml.

Laboratory Studies. The failure of natural water studies to detect glycolate led to a study of glycolate excretion in the laboratory. Six algal cultures were obtained for a study of extracellular glycolic acid production by algae under controlled laboratory conditions. The cultures and their sources are listed.

The first two cultures were obtained and maintained as unialgal cultures while the remaining four cultures were ob-

Chlorella pyrenoidosa. Wisconsin No. 2005, G. P. Fitzgerald, Project Associate, University of Wisconsin, Madison, Wis.
Chlorella pyrenoidosa (Emerson strain). Kettering Laboratory, T. E. Brown, Kettering Laboratory, Yellow Springs Ohio.
Chlorella pyrenoidosa (Emerson strain). Texas No. 78712, J. Meyer, University of Texas, Austin, Tex.
Chlorella pyrenoidosa (Emerson strain). Indiana No. 251, R. C. Starr, University of Indiana, Bloomington, Ind.
Chlorella pyrenoidosa (Emerson strain). Indiana No. 252, R. C. Starr, University of Indiana, Bloomington, Ind.
Chlorella pyrenoidosa (Emerson strain). Indiana No. 395, R. C. Starr, University of Indiana, Bloomington, Ind.

tained and maintained as bacteria-free pure cultures. The culture media selected for these experiments were Gorham's (Hughes, Gorham, *et al.*, 1958) and Chu's No. 10 media (Chu, 1942). Since nitrate interferes with the glycolate analysis in the Calkins procedure, the two media were modified by substitution of ammonium chloride for the sodium nitrate as the nitrogen source. All algal cultures received for glycolate experiments were immediately subcultured by mass transfer of cells to six sterile Gorham's agar slants. These cultures were placed in the light (180 foot candles) and incubated in a constant temperature culture room ($23^{\circ} \pm 1^{\circ}$ C.). After sufficient growth, these subcultures were used as stock cultures for the laboratory glycolate excretion experiments.

For this series of experiments, cells were grown in 30-ml. portions in 50-ml. Erlenmeyer flasks. After a heavy growth was attained, a 5-ml. aliquot of the suspended cells was taken with a sterile 10-ml. disposable syringe and injected through a serum cap into a 27-liter culture flask containing 1000 ml. of culture media. The culture was then placed in a controlled temperature culture room ($23^{\circ} \pm 1^{\circ}$ C.) in the light (700 foot candles) and mixed once daily by swirling. Samples were taken at various times and analyzed directly for glycolate content. The results of these experiments are given in Table I. Significant glycolate concentrations were recorded for the Texas, Kettering, and Indiana No. 252 culture after three to four days' growth. The remaining cultures showed glycolate accumulation at some time during the experiment but to a

much lesser extent. This variability in extracellular glycolate accumulation by algae of the same species and strain designation points out the difficulties encountered in extrapolating laboratory data to field situations.

An aliquot of culture II, Indiana No. 252, was subjected to the ion exchange chromatography procedure as described by Palmer (1955). This method showed recovery of 6.75 mg. per liter, while the direct analysis showed glycolate to be present in a concentration of 7.5 mg. per liter. This experiment provided indirect evidence in substantiation of the ion exchange procedure used in the natural water study and also verified the presence of glycolate in the laboratory cultures.

Discussion

This investigation has shown that none of the Madison lakes contained detectable concentrations of glycolate during the period of study. These data are in agreement with those of Anita, McAllister, *et al.* (1963) who could only detect the possible presence of glycolate in one sample during a 100-day study and those of Hellebust (1965) who reported no glycolate in his concentrated surface water samples. However, they do not agree with the data of Fogg and Nalewajko (1963) who reported detectable concentrations of glycolate in the majority of their samples.

It is concluded that glycolate is not present universally in natural water in substantial quantities. The hypothesis that extracellular glycolate concentration in natural water represents a controlling factor with respect to the initiation of exponential algal growth cannot be confirmed.

Acknowledgment

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Table I. Long-Term Extracellular Glycolate Accumulation (Mg./Liter)

Strain	Culture Age, Days					
	3	4	6	7	10	17
Wisconsin	* ^a	*	2.5	1.5	1.5	*
Wisconsin	*	*	2.5	+ ^b	+	*
Kettering	4.5	5.5	6.0	5.0	5.0	... ^c
Kettering	2.0	2.5	2.0	2.5	2.5	...
Texas	...	6.5	7.0	7.5	7.0	2.5
Texas	...	1.0	2.5	+	+	4.5
Indiana 251	...	2.0	1.0	1.5	2.0	*
Indiana 251	...	*	+	+	+	*
Indiana 252	...	6.5	4.5	5.0	4.5	2.0
Indiana 252	...	7.5
Indiana 395	...	*	1.0	+	3.0	...
Indiana 395	...	1.0	*	1.5	1.5	...

^a * denotes below detectable limit of test.

^b + denotes color developed but insufficient for absorption reading.

^c ... denotes no test made on sample.

BOOKSHELF

The wide world of nuclear desalination

Water Production Using Nuclear Energy. Edited by R. G. Post and R. L. Seale. A symposium. ix + 396 pages. University of Arizona Press, College Station, Tucson, Ariz. 85700. 1966. \$7.50, hard cover. *Everett D. Howe is in the department of mechanical engineering, University of California, Berkeley*

By *Everett D. Howe*

Based on a symposium held at the University of Arizona in March 1965, this book contains 27 papers by different authors. The papers are grouped into six fairly homogeneous sections. The particular use of nuclear energy dealt with in these articles is the application of nuclear fuels to the generation of heat in reactors and the subsequent use of this heat in distillers. So far as distillers are concerned, heat energy from nuclear reactors is used in exactly the same manner as heat energy from any other source. Since the cost of the heat energy is a major portion of the cost of producing distilled water, the point of interest in nuclear reactors for heat production is that these devices give greater promise of cheaper heat energy than any other device.

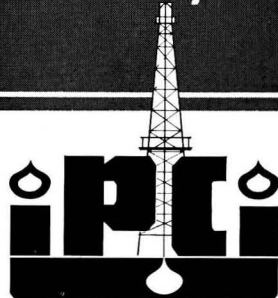
The symposium on which the book is based was held soon after the publication of the first engineering report on the proposed Mw./day dual-purpose nuclear desalination plant at Los Angeles. One paper near the end of the book is devoted to comments on the above report and was written by a representative of the Bechtel Corporation, which prepared the report. Since the Bechtel report was the first definitive study to be made of a nuclear desalination plant for a specific location, there are frequent references to it throughout the book.

Water inventory

The book opens with a section stating the availability of and the need for water in the United States and Canada, together with an indication of the role of the Atomic Energy Commission in the desalting field. It is argued that the technologies of desalination and nuclear energy usage are based on common scientific disciplines and that the knowledge acquired in nuclear developments will be valuable to desalination. An inventory of surface and underground supplies of fresh water in North America is presented, together with an estimate of future water needs. It is shown that shortages of water in certain parts of the U.S. are likely to develop in the next 20 to 40 years, and that desalination is one of the more promising schemes for overcoming the shortage. The possible use of desalination in Mexico is dealt with in a paper which describes the new national research facility and outlines the proposed U.S.-Mexico cooperative dual-purpose desalination plant designed to benefit California, Arizona, Sonora, and Baja California.

A section devoted to the sociological problems of water production begins with a presentation of the NAWAPA plan—the North American Water and Power Alliance concept advanced by Ralph M. Parsons Co. This imaginative proposal involves a system of dams, aqueducts, tunnels, and pumping plants which would be used to collect water from Alaskan and Canadian watersheds and rivers. The water would then be distributed in the U.S., Canada, and Mexico. The estimated cost of \$100 billion indicates the magnitude of the plan, and its international character will require full consideration of the economical, sociological, and ecological aspects.

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The second paper in this section deals with the legal aspects of water supply and concludes that the variety of laws presently in force is great enough to cover the use of desalted water.

Economic viewpoint

While most of the papers in the book are favorable to desalination in general, and to nuclear desalination in particular, there are two papers written by economists which urge caution in applying desalination to the solution of water supply problems. In considering the dual-purpose scheme, as exemplified by the Bechtel engineering report, it is pointed out that the water costs estimated for such plants are too high for economic justification. Attention is called to the lack of consideration in engineering studies of such factors as national energy policies, technological discontinuities in reactor and distiller development, and possible increases in interest rates. While admitting that these factors cannot be included in engineering design studies, the economists urge that they should be used as deterring influences in the face of over-optimistic proposals for large plants.

In a further section of the book, desalting technology is explored in terms of experience with the OSW demonstration plants at Freeport, Tex. and Point Loma, Calif., and the pilot plants at the OSW East Coast Test Facility, Wrightsville Beach, N.C. In each case there is an illuminating discussion of difficulties encountered and corrective measures adopted. Also included is a discussion of the performance of the electro dialysis plant at Buckeye, Ariz., in which the significance of a highly variable demand for water is brought out. Annual load factors decreased from 48% with saline water to 27% with demineralized water, with resultant increases in water cost. This section closes with a brief discussion of a process for regenerating ion exchange resins by changing resin temperatures, and leads to suggestions for a demineralizing process in which ion exchange is combined with multi-effect distillation.

The impact of new water sources is considered in terms of problems introduced by the disposal of hot concentrated brines from desalting plants. The often repeated suggestion of re-

covering salable chemicals is reviewed, and it is concluded that recoverable materials present little promise for reduction in water cost through chemical byproduct sales. Thermal and nuclear pollution are discussed in terms of existing power and nuclear processing plants. It was proposed that a case study of the three factors of radioactivity, salinity, and temperature of waste brines be made in conjunction with the early years of operation of one or more large nuclear desalination plants. A rough figure for the cost of such a study was placed at \$5 million, which would be spread over the useful life of the plant, adding about one cent per thousand gallons to the cost of water produced in a 50 m.g.d. plant.

Balanced systems

Another possible impact of new sources of water is the concurrent production of power, water, and agricultural commodities in a closely coordinated fashion. Experience with solar distillation at Puerto Peñasco (Mexico) and with greenhouse production of food led the University of Arizona group to propose a one-acre installation, said to be capable of furnishing 60 kw. of electric generating capacity, 2.5 m.g.d. of water, and 100 tons of vegetable products per year, regarded as adequate for 500 people. For much larger groups of people, balanced systems of this character would need power supplies large enough to warrant nuclear reactors.

Detailed reviews of the potential usefulness of several reactor types are presented. There are discussions of a water-cooled graphite-moderated concept, a heavy-water moderated, organic-cooled reactor, a liquid-metal cooled fast breeder reactor, and a high temperature gas-cooled reactor, as well as the boiling water reactor presently so extensively used for electric power generation. There seems to be general agreement that one or more of these concepts could be expected to result in low-cost heat energy when used in a 3500 Mw. reactor by 1980.

Discussions of large-scale systems available for desalting water begin with a paper by D. P. Hammond urging the use of nuclear desalination for agricultural water. Using graphs to show the variation of capital costs

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NEW PRODUCTS, NEW LITERATURE:

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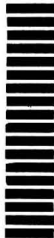
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with performance ratios for the several elements of a distillation plant, and estimates for power and labor costs, Hammond concludes that agricultural water costs would be as low as \$28 per acre-foot. These low costs would require substantial but expected improvements in very large single-purpose plant concepts, in low-cost but efficient distillers, and in the cost of heat from nuclear reactors.

Other papers in this group examine both water-only and dual-purpose plant concepts. Water-only designs consider a distiller capable of using a maximum brine temperature of 400° F., compared with about 250° F. in present units, and a deep-pool reactor in which the coolant reaches a maximum temperature of 270° F., compared with about 1000° F. in present power reactors. It is concluded that the single-purpose plant would produce more expensive water than that from the dual-purpose plants, but that further development in the two concepts noted above should substantially reduce the difference between water costs from the two types of plants. A presentation by the designers of the Mw./day plant at Los Angeles gives some of the background for the design features of that plant, and answers some questions which have been raised regarding this proposal.

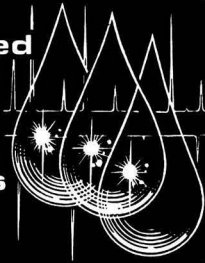
Land subsidence

The final paper in this collection deals with the Texcoco project for supplying water and power to Mexico City, and in so doing, reducing the city's problem of land subsidence. The general scheme is to substitute desalted saline ground water from the nearby Texcoco valley for the potable water now being withdrawn from the clay beneath Mexico City. Cessation of this withdrawal is expected to prevent the collapse of the spongelike clay under the city, and thereby prevent further subsidence.

In conclusion, this book covers the subject of nuclear desalination very broadly. About half of the book is devoted explicitly to technical matters involved in desalination and in nuclear reactors. The other half is taken up with the justification of desalination, and with peripheral matters. The two papers on economics

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seem particularly appropriate for inclusion in this book, since too little has been written on desalination by economists. The papers on the NAWAPA plan and the combined food-water-power plant seem to be less pertinent to nuclear desalination than the other papers are. ■

Chemical Markets in Water and Wastewater Treatment. iii + 80 pages. Environmental Science Services Corp., 750 Summer St., Stamford, Conn., 06902. \$20, paper.

This report examines the status of federal and state legislation on water pollution control and water treatment, and the impact of this legislation on treatment requirements and the market for treatment chemicals. The chemicals are discussed in three groups by their use—for treatment of waste waters, industrial process waters, and municipal waters. The report also includes present and estimated future use patterns for 80 bulk and specialty chemicals used in the water and waste water treatment markets. ■

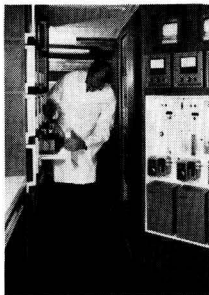
The CRC Handbook of Chemistry and Physics, 49th Edition. Edited by Robert C. Weast and Samuel M. Selby. 2070 pages + 19-page index. The Chemical Rubber Co., 18901 Cranwood Parkway, Cleveland, Ohio 44128. \$19.50, hard cover. ■

New ES&T Staff Member Appointed



Carol Ann Goode has joined the staff of ES&T as an editorial assistant. She will devote her efforts to editing material for the staff-generated portions of ES&T. Miss Goode comes to ES&T from the Barton-Gillet Company in Baltimore and New York, where she was responsible for their proofreading and copy editing operations, and acted as liaison between the art and production departments. Previously (1963-1965), she was on the technical services staff of the Johns Hopkins University Library. Miss Goode received her B.A. in speech and drama, with a chemistry minor, from the College of Notre Dame of Maryland (1961), and completed two years of graduate study at the University of Maryland (1961-1963).

NEW PRODUCTS DIGEST



Touring Sales Lab

A mobile laboratory contains instruments representative of the company's air and water measurement capabilities. Following a stop at the Air Pollution Control Association's annual meeting in St. Paul (Minn.), the mobile lab started on a nationwide tour. Along with the display of instruments,

Beckman has laid plans for symposia that will be conducted by company specialists on air and water quality. The symposia will include presentations on the current status of air quality analysis methods, and a session on calibrating air quality analyzers. Beckman Instruments, Inc. **61**

Scale Inhibitor

A water soluble additive prevents sludge from becoming scale in the alkaline cleaning of ferrous metals. Drumite eliminates down time normally needed for removing scale by hand scraping or acid soaking, and also extends the life of nozzle heads. With Drumite, washing tanks can be recharged with less cleaning compound. Gillette Inhibitor Co. **62**

Submersible Pump

A submersible pump can handle 6000 gallons of water per hour and has a total head capacity of 46 feet. Called the Mini-Merse, the pump is 15 inches high, 8 1/4 inches in diameter, and weighs 28 pounds. The pump is powered by a 1/2-hp., 110-volt motor with built-in contractor which eliminates the need for external starter and controls. ITT Marlow. **63**

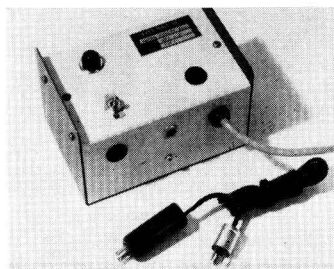
Temperature Test Chamber

A bench-type temperature test chamber with a range of -95° F. to 350° F., has a control tolerance of $\pm 1/2^\circ$ throughout the range. It features an all-welded, fully hermetic, single-stage air-cooled refrigeration system. The compact Tenney SST chamber measures 36 inches wide by 26 inches high by 21 inches deep, and has a work area of 2100 cubic inches. Tenney Engineering, Inc. **64**

Liquid Level Measurements

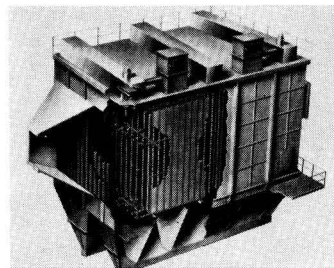
Hydrogauge, a beam-balance instrument designed to measure accurately liquid levels or depths, can be used to determine the depths of rivers, reservoirs, precipitation standpipes, underground water tables and snow pillow standpipes. The instrument, which is suited to a variety of tank-installations, has a traveling poise weight positioned

by a motor to create the appropriate balancing moment. The Hydrogauge is suitable for field use in remote unpopulated areas. Statham Instruments, Inc. **65**



Water Purity Indicator-Controller

Model WPI-2 Water-Purity Indicator-Controller shows deviation from preset water purity in deionized water systems. In addition, control contacts are automatically actuated to supply power for corrective equipment and alarm devices. All components and circuits except the replaceable electrode cells are included in a single 6 x 3 1/2-inch housing. Sever-Hall. **66**



Electrostatic Precipitators

The Series 1200 electrostatic precipitators are said to have widespread application in industrial gas cleaning and municipal air pollution control. The series features a number of improvements, among which are the following: a suspended-insulator system enclosed

in a pressurized area; discharge electrodes which permit a superior corona effect and which can be placed in an offset axis so as to operate at higher voltages; and a collector electrode design which provides turbulence-free catch openings greater than 80% without permitting the precipitated dust to be re-entrained into the gas stream. Airetron Engineering Corp. 67



Temperature Indicator

Temperatures can be read accurately in difficult situations in the plant, laboratory, or field with the Mark Ten Temperature Indicator. Remote readings—which can be made 60 feet deep or 60 feet distant—are made by a drum cable assembly that is an integral part of the instrument. Battery operated and weighing less than 1 pound, the Mark Ten has a standard range of 0° F. to 212° F. Vexilar Engineering Co. 68

Portable Gas Leak Detector

Model 21-200 portable gas leak detector is designed for simplicity of operation and rough handling in remote or field locations. The unit, which weighs 8 pounds and is about the size of a cigar box, will detect light or heavy gases (inert or combustible) in hot or cold systems or storage tanks. Available with audible and visual signal detection systems. Gow-Mac Instrument Co. 69

Wind Measurements

Model 1149700 wind converter recorder and model 1141664 wind speed and direction indicator with direction potentiometer, are designed for use in air pollution control activities. The units provide visual, permanent chart records and outputs suitable for data processing. Bendix Corp. 70

Water Quality Monitor

Model 1410 water quality monitor measures dissolved oxygen, chlorides, pH, turbidity, temperature, conductivity, oxidation-reduction potential, hardness, total carbon, and many specific ions. Measurements can be displayed on a strip chart recorder, punched on tape, or telemetered to distant points. The unit features a swing-out self-cleaning flow chamber, solid state electronics, and a thallium electrode membraneless dissolved oxygen probe. Union Carbide Corp. 71

Cold Rooms

A line of constant temperature walk-in rooms is designed for research at 4° C. and -20° C., the two most commonly used cold room temperatures. MINER (Minimum Increment Narrow range Environmental Research) rooms are factory preset, requiring no additional calibration, and temperatures can be controlled to $\pm 0.01^\circ$ C. A visual and audible alarm system provides safety control, should temperatures exceed control settings. Rooms are made of sectionalized panels mechanically locked in place from the interior. Sizes available range from 6 to 12 feet wide and 4 to 14 feet deep. Hotpack Corp. 72

CO Detector Tube

Model 100 of the company's length-of-stain carbon monoxide detector tube is accurate to $\pm 10\%$ of values obtained with an infrared analyzer, and results are always reproducible, according to the manufacturer. The $\frac{3}{8}$ -inch long length-of-stain is produced with one stroke of the model 400 precision gas pump (100 ml.), and is accomplished in three minutes. Union Industrial Equipment Corp. 73

Test Tube Holder

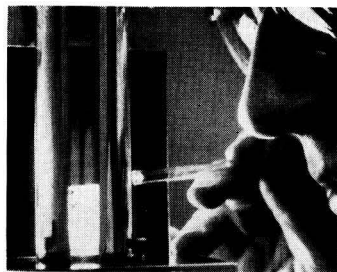
A transparent plastic (methacrylate) test tube holder firmly supports tubes in a vertical position. So firmly are the tubes held that they can be used with magnetic stirring techniques that use a micro stirring rod. The holder, which can accommodate tubes from $\frac{1}{2}$ -1 $\frac{1}{4}$ inch o.d., is especially suitable for microbial culturing, because the contents of the tube are visible. Chemical Rubber Co. 74

Ozonizer

A line of continuous duty ozonizers weighing 1-22 kg. and producing 25-1000 mg./hr. of ozone, is available. The units produce 500 p.p.m. ozone on dry air feed, and 1000 p.p.m. ozone from pure oxygen feed. Ozonizers are used in color fading and degradative testing of textiles, paper, rubber, and other natural and synthetic polymers; in fresh water and marine life support systems, where they reduce bacteria counts; in transport and processing of shellfish; in upper atmosphere simulation; and in medical and veterinary experiments. Triton Aquatics, Inc. 75

Water Purity Indicator

Model WPI-2 water purity indicator-controller has an indicator lamp that stays lighted when quality of a de-ionized water stream is above a preset level. The lamp goes off when water purity falls below the preset level. Control contacts (to supply power for corrective equipment or alarm devices) are automatically actuated. A thermal time delay can be set for 1-180 seconds delay. All components and circuits except the replaceable electrode cell are included in the single housing. Sever-Hall, Inc. 76



Desalination by Freezing

A technique to make freezing water self-cleaning (during processes that desalt water by turning it into pure ice) employs a vacuum to work up a froth in the naturally air-saturated layer of water just in front of the advancing ice. Called "bubble scrubbing," the process prevents the entrapment of whole droplets of brine within the ice, a phenomenon which has plagued freezing processes for desalination. Westinghouse Electric Corp. 77

NEW LITERATURE DIGEST

Water management. A 4-page brochure details Waste Audit, a systems approach to management of water pollution problems. A Waste Audit helps to determine and implement a full range of management programs including sampling systems, analytical measurements, monitoring instrument alarm devices, computer analysis, and data retrieval. The folder describes Waste Audit, what it provides industrial management, and how it works. Cyrus Wm. Rice and Co. **91**

Foundry pollution problems. Dust control and air pollution abatement in the foundry industry are the subjects of a 6-page brochure. It describes the major sources of contaminants (including melting, sand preparation and handling, and metal cleaning and finishing) as well as dust and fume collection equipment to remove these contaminants. Ducon Co., Inc. **92**

Dust/mist collectors. In capsule form, this 8-page folder covers the operating ranges and recommended uses for various dust collectors and mist collectors, as well as pertinent information on tube type after-filters. Agat Manufacturing Co. **93**

Industrial waste. An 8-page catalog (WC-139) describes industrial waste treatment equipment and systems, lists technical reprints available, and includes a partial listing of industrial waste treatment installations. Graver Water Conditioning Co. **94**

Modular mass spectrometer. Bulletin 21621 is a 16-page brochure describing a line of modular mass spectrometers for university, industrial, research, and biomedical laboratory applications. The bulletin presents a variety of basic vacuum, analyzer, inlet system, and cabinetry modules. Bell & Howell Corp. **95**

Waste treatment. Industrial waste treatment concepts and practices are summarized in an 8-page brochure (Technical Paper 215). The brochure covers conventional methods of mechanical, chemical, and biological treatment for waste water control. Research on tertiary waste treatment and plant design are also covered. Betz Laboratories, Inc. **96**

Polymers. A 16-page booklet, "Guide to Polymer Properties," compares physical properties and chemical resistance of various rubber polymers. A chart comparing natural rubber with the six most frequently used synthetic rubbers is included. Uniroyal, Inc. **97**

Centrifugal gas scrubbers. Bulletin 609 is an 8-page brochure on centrifugal gas scrubbers. The bulletin describes the operation and advantages of this type of gas scrubber, and provides data to substantiate the manufacturer's claim of 98-100% efficiency on all particles exceeding 5 microns. Universal Oil Products Co. **98**

Thunderstorms. Stay indoors and keep calm during thunderstorms, advises a new 6-page pamphlet, "Thunderstorms," which describes an average day in July when, "in 18 states, eight persons were injured and two were killed, and some \$5 million in property damage was done by . . . thunderstorms." 15 cents. Environmental Science Services Administration, U.S. Department of Commerce, Washington, D.C. 20230. (Write direct.)

Pesticides. A 12-page pamphlet, "Fish, Wildlife, and Pesticides," discusses pesticide use and its effect on the food chain phenomena. The pamphlet also discusses residue concentrations and the effects pesticides have on reproduction of fish and wildlife. Steps for safe pesticide use are proposed. 10 cents. Another pamphlet (2 pages), "Questions and Answers on the Use of Pesticides," explains pesticide registration,

persistence, and like topics. Fish and Wildlife Service, U. S. Department of the Interior, Washington, D. C. 20240. (Write direct.)

Occupational diseases. A 9-page pamphlet called "Occupational Disease . . . The Silent Enemy" describes various health hazards on the job, such as dusts, chemical fumes, noise, and excessive heat and cold. The pamphlet also contains a list of questions designed to help determine whether there are health hazards on a particular job, as well as a list of protective measures to be taken. Copies may be obtained from Bureau of Disease Prevention and Environmental Control, Public Health Service, Washington, D.C. 20201. (Write direct.)

Simulation of waste water renovation systems. "Preliminary Design and Simulation of Conventional Wastewater Renovation Systems Using the Digital Computer" brings together in one computational scheme the significant cost and performance relationships for a group of processes. The 90-page report (WP-20-9) calculates the performance and cost of the system as a whole, based on relationships developed for the processes individually. A copy of the report, part of the Water Pollution Control Research Series, may be obtained from the Publications Office, Ohio Basin Region, Federal Water Pollution Control Administration, Cincinnati, Ohio 45226. (Write direct.)

Removal of strontium from milk. "Full-Scale System for Removal of Radiostrontium from Milk" is the proceedings of a seminar held in February 1965 at Lebanon, Mo. A free copy of the 100-page report, PHS Publication No. 999-RH-28, is available from the Office of Information, National Center for Radiological Health, Public Health Service, Rockville, Md., 20852. (Write direct.)

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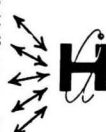
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MEETING GUIDE

July 1-August 30 Engineering Foundation Research Conferences

Wayland Academy, Beaver Dam, Wis.

University School, Milwaukee, Wis.

Proctor Academy, Andover, N.H.

University of California, Santa Barbara, Calif.

Sixteen one-week conferences will include sessions on engineering aspects of solid waste research, world food supplies, behavioral sciences, urban hydrology, air pollution, and oceanography. Attendance is limited; for further information contact Engineering Foundation, 345 E. 47th Street, New York, N.Y. 10017.

July 7-11 American Electroplaters Society Annual Convention

San Francisco, Calif.

As part of its convention, the American Electroplaters Society will hold a technical program on related air pollution problems. Further details from General Manager, American Electroplaters Society, 443 Broad St., Newark, N.J. 07102

July 8-12 American Society for Testing and Materials

International Conference on Air Quality Criteria

Goddard College, Plainfield, Vt.

Sponsored by ASTM's Committee D-22 on Methods of Atmospheric Sampling and Analysis, the meeting will include discussions on problems and philosophy of air quality, and the relationship of criteria to analytical methodology needed. Attendance is limited to 100 practitioners. Contact Prof. P. M. Giever, School of Public Health, University of Michigan, Ann Arbor, Mich. 48104

July 20-August 10 Polytechnic Institute of Brooklyn

Short Course on Research Instrumentation

333 Jay Street, Brooklyn, N.Y. 11201

Laboratory course in basic electronics and instrument techniques for engineers, physical and biological scientists, and science educators. Contact Prof. Kenneth R. Jolls, (212) 643-4442

July 22-24 American Medical Association and Others

Air Pollution Medical Research Conference

Denver Hilton Hotel, Denver, Col.

Session topics will be problem formulation and analysis, epidemiological relationships, pathogenic role of atmospheric pollutants, animal toxicology, biochemical effects of air pollutants, emphysema, and acute effects in man.

July 22-24 University of Rhode Island, College of Engineering

Annual Northeast Regional Anti-Pollution Conference

University of Rhode Island, Kingston

Conference will cover pollution problems in the northeast and suggested solutions. Sessions are planned on waste water, air pollution, and solid waste disposal.

July 29-August 2 Instrument Society of America

Research Conference on Instrumentation Science

Quinnipiac College, Hamden, Conn.

Session topics include doppler ultrasound for medical diagnosis, energy sensing transducers, fluidics, direct sensors and system performance, computer challenge to the accuracy of sensors, ultra high vacuum measurement, analytical instrumentation, and remote data read-out systems.

August 18-21 Soil Conservation Society of America

23rd Annual Meeting

University of Georgia, Athens

This year's meeting, theme of which is "Creative Conservation for Life and Living," will feature discussions on natural resources and man's environment, economics of environmental modification, land, air, and water conservation, and recreational needs in land and resources.

August 20-21 North Atlantic Regional Water Resources Study

Sheraton Belvedere Hotel, Baltimore, Md.

NAR's Coordinating committee, a 23-member panel of federal and state water resources officials, will hold a public meeting on NAR study of water and related land resources of Atlantic seaboard states. Additional meeting planned for Oct. 22-23 at Willard Hotel, Wash., D.C.

August 26-30 International Atomic Energy Agency

Operating and Developmental Experience in Treatment of Airborne Radioactive Waste

United Nations Building, New York, N.Y.

Symposium will discuss recent R&D in treatment of nuclear energy wastes, with review of operating experience. Separate one-day session for U.S. papers will be designated "Tenth AEC Air Cleaning Conference." Further Details: Mr. John Kane, Chief, International Conferences Program, Division of Technical Information, Atomic Energy Commission, Wash., D.C. 20545

September 3-7 American Institute of Biological Sciences

19th Annual Meeting

Ohio State University, Columbus

Meeting will include symposia, panel discussions, field trips, and workshops conducted by member societies. Features include symposium on biological effects of nuclear excavation of a sea level canal, round-table discussion of information problems in biological sciences, and an AIBS plenary session on the biologist's role in the world food crisis.

September 22-27 Water Pollution Control Federation

Annual Conference

Conrad Hilton Hotel, Chicago, Ill.

Technical program includes sessions on federal-state relationships, combined sewers, nutrient removal, water quality analysis, manpower and education crises, and water resources planning.

September 25-27 Association of Analytical Chemists

16th Detroit Anachem Conference

Statler Hilton Hotel, Detroit, Mich.

Program of invited and contributed papers will include separate session on environmental chemical analysis. Manufacturers' exhibit will feature latest developments in scientific instrumentation.

October 8-10 Oak Ridge National Laboratory

Conference on Analytical Chemistry in Nuclear Technology

Mountain View Hotel, Gatlinburg, Tenn.

This year's conference will highlight the role of the analytical chemist in research on production and chemical properties of the actinide elements and the solution of problems in the field of environmental pollution.

(Meeting Guide continues on page 570)

October 22-25

Technical Association of the Pulp and Paper Industry

Secondary Fiber Pulping Conference

Sheraton Dayton Hotel, Dayton, Ohio

Theme of this TAPPI conference is "Waste Treatment and Disposal of Secondary Fiber." Among the topics of papers at the technical sessions are sludge treatment, centrifugal dewatering, municipal and industrial waste treatment, and utilization of waste water and sludge.

November 19

University of Missouri College of Engineering and Air Conservation Commission of Missouri

Air Pollution Control—SO_x

University of Missouri, Columbia

One day session for technical and management personnel and interested lay persons concerned with air pollution control. Detailed program available Sept. 1 from Extension Division, Whitten Hall, University of Missouri, Columbia, Mo.

November 21-22

Franklin Institute and the National Center for Air Pollution Control

Symposium on Heterogeneous Catalysis for Control of Air Pollution

Franklin Institute, Philadelphia, Pa.

Speakers will explore and delineate the role of catalysis in air pollution abatement and fuel cell applications. Further information from Gordon P. Larson, Environmental Resources Center, Franklin Institute Research Laboratories, Philadelphia, Pa. 19103

September 17-24, 1969

Czechoslovak Academy of Sciences and Austrian Academy of Science

International Conference on Condensation and Ice Nuclei

Prague (Sept. 17-20), Vienna (Sept. 22-24)

Topics to be discussed are the physics and physical chemistry of aerosol nucleation, methodology of measurement of condensation and ice nuclei, and condensation and ice nuclei in cloud formation. Further information from Dr. J. Podzimek, Institute for Physics of the Atmosphere, CSAV, Bocni II, Praha-Sporilo, Czechoslovakia, or Prof. O. Preining, 1st Physics Institute of the University of Vienna, Strudlhofgasse 4, A-1090, Vienna, Austria.

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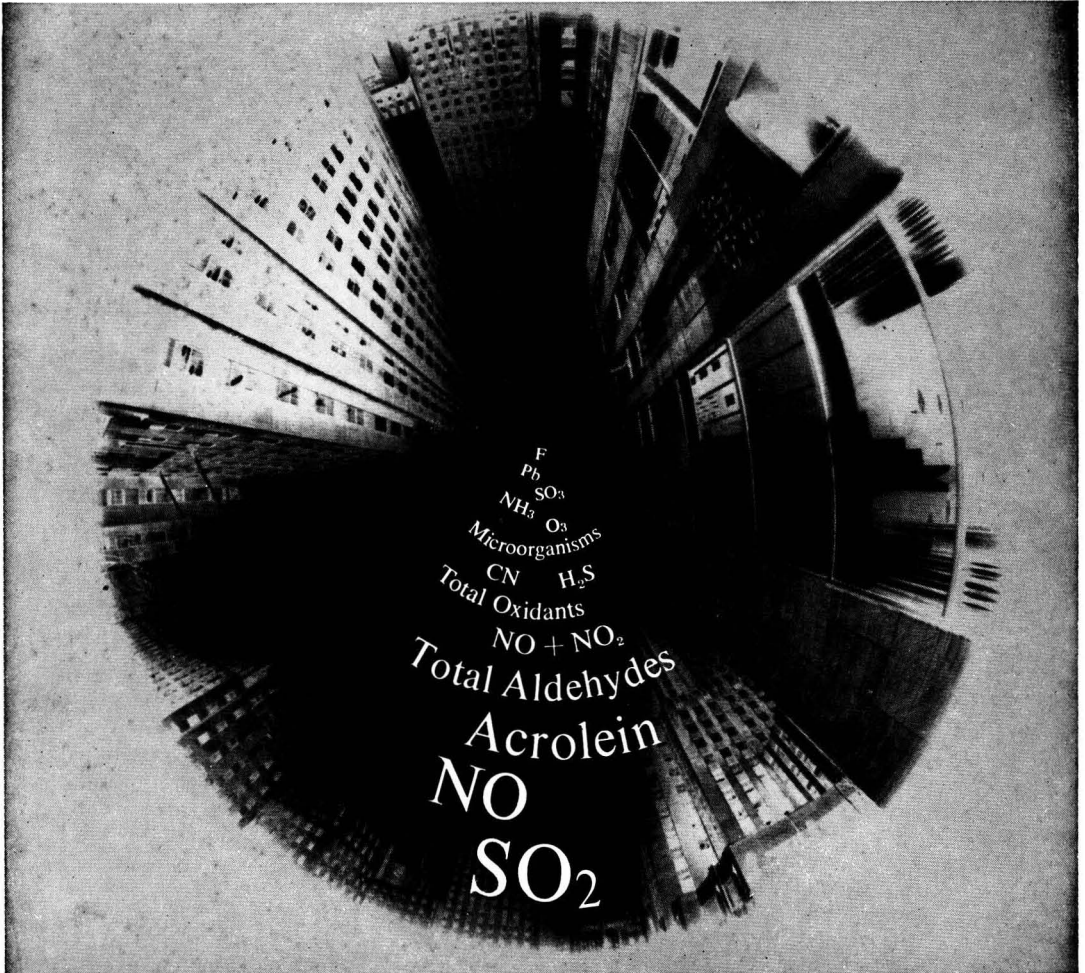
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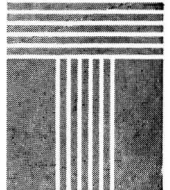
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