ENVIRONMENTAL Science & Technology

Emphasizing
Water,
Air, &
Waste
Chemistry

FEBRUARY 1969

MORE U.S. FUNDS FOR POLLUTION ABATEMENT 113

Monitoring air pollution is now a 4-dimensional problem

To measure, control and ultimately reduce gaseous and particulate contamination of the air around us, today's meteorologist and industrial process engineer need tools which will rapidly and accurately measure many parameters — and supply data which are easy to interpret and use. Such a "tool" is Climet's new Digital Data Collection System: at preset intervals it automatically samples, digitizes and records on computer-compatible punched tape up to 10 parameters — such as wind speed and direction, SO_2, CO and NO_2 concentrations. Significant amounts of data are presented with 0.1% accuracy along with the vital additional parameter of time.

The interest this $6000 Climet CI-100 system generated at the recent Air Pollution Control Association meeting in St. Paul attests to its practicality of design and application . . . and typifies one of several ways EG&G is applying modern technology to problems in the environmental sciences. Through the individual yet complementary skills of four EG&G companies — augmented by EG&G's long-established systems development proficiency — realistic solutions to multi-discipline problems can be achieved with consistent thoroughness. Bollay Associates are recognized authorities in air and water resources management, particularly in cloud physics, diffusion and air-sea interface studies . . . Cambridge Systems and Climet Instruments provide advanced yet practical systems and sensors for hygrometry, thermometry and anemometry measurements related to meteorological and air pollution studies . . . Geodyne instruments and systems measure and analyze oceanographic and undersea phenomena. To know more about how one or several of these EG&G companies can help you in your particular environmental science efforts, call or write, C. Robert Paulson, EG&G Environmental Sciences, Crosby Drive, Bedford, Mass. 01730 (Tel. area 617: 271-5519).

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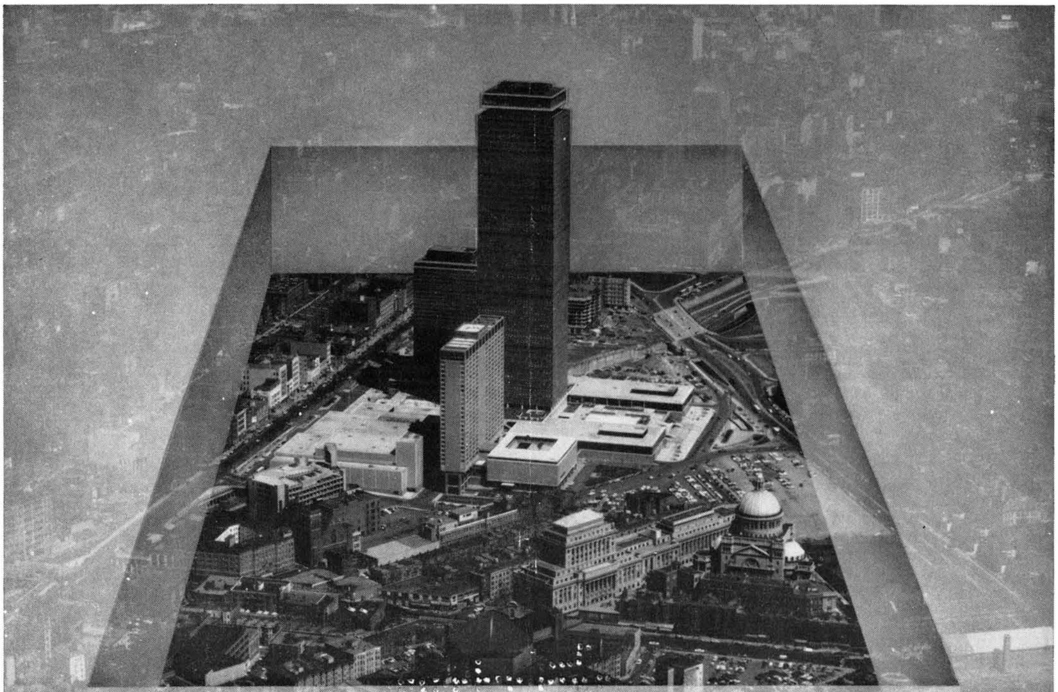

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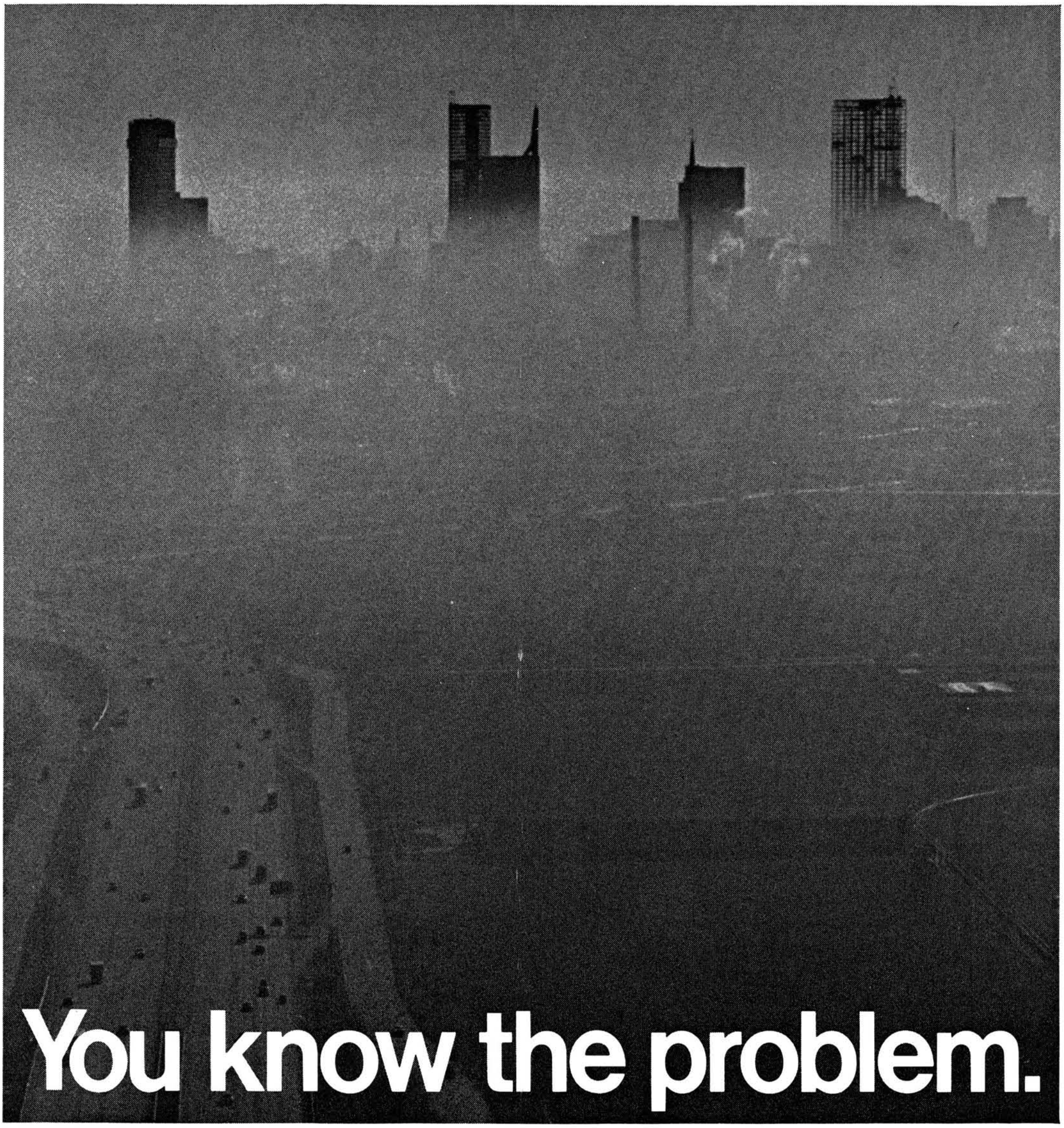

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Volume 3, Number 2
February 1969

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Current Research

Computational analysis of transient response to quantitative shock loadings of heterogeneous populations in continuous culture 143

F. F. Storer and A. F. Gaudy, Jr.

Shock loadings of pollutants disrupt the steady state operation of the activated sludge process. A threefold increase in the feed concentration—the concentration of carbon in the inflowing waste—to heterogeneous microbial populations of sewage origin which were grown under aerobic conditions in a mixed reactor did not produce a constant value for cell yield. Nevertheless, a growth rate hysteresis curve was obtained from the data.

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F. K. Kawahara

The identity of oil pollutants in surface waters yields to a new analytical technique. Analysis of beach water samples from the 1967 Lake Michigan oil spill reveal that the two pollutants—residual fuel oil (No. 6 fuel oil) and asphalt—can be differentiated by a rapid infrared technique which involves a comparison of several wave number ratios.

A new instrument for the evaluation of environmental aerocolloids 154

A. Goetz

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Application of internal reflectance spectroscopy to water pollution analyses 161

J. S. Mattson and H. B. Mark, Jr.

Opaque aqueous samples of marine sediments, water filtrates, aqueous suspensions, and the like can be analyzed by an internal reflectance spectrometric technique. More rapid than conventional techniques which require homogeneous transparent solutions, the present technique is used to identify organic components of optically opaque materials, for example, such systems as the solid materials in cigarette smoke, waters containing blue-green algae, and Lake Erie mud bottoms.

Application of semipermeable ion exchange membranes to in situ determination of trace metal ions in aqueous systems by electrochemical and neutron activation techniques. A critical evaluation of these techniques 165

H. B. Mark, Jr., U. Eisner, J. M. Rottschafer, J. S. Mattson, and F. J. Berlandi

Ion exchange membranes can be positioned in natural water systems where the membranes serve as in situ preconcentration matrices for trace metal ions. The membranes are then removed and analyzed for trace metal ions—for example, Ag^{+}, Cu^{+2}, Zn^{+2}, Co^{+2}, and In^{+3}—by neutron activation analysis or anoidic stripping voltammetry. The technique is not practical for routine trace analysis, and long times are required for equilibration of the membranes with their water systems.

Communications

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H. O. Smith and A. D. Hochstettler

Minimum identifiable odor levels offer a more reliable method for determining airborne organic compounds than adsorption of the compounds on surfaces. Minimum identifiable odor levels for styrene, chlorobenzene, and chloroacetic acid, as determined by a panel of seven judges, are shown.

Levels of stable strontium in milk and the total diet 171

G. L. Rehnberg, A. B. Strong, C. R. Porter, and M. W. Carter

Levels of stable strontium in pasteurized milk and total food diets for each month in 1965 are reported for the 20 stations in the Southeastern Radiological Health Laboratory's pasteurized milk network and institutional total diet sampling network. For milk, data from the 20 stations averaged 0.86 ± 0.23 mg. of Sr^{+2} per liter and ranged from a low value of 0.43 ± 0.03 (Washington, D. C.) to a high value of 1.51 ± 0.11 (Cristobal, Canal Zone). For total diet, data from the network averaged 0.89 ± 0.18 mg. per Kg. wet weight and ranged from a low value of 0.49 ± 0.02 (Charleston, S. C.) to a high value of 1.96 ± 0.10 (Oklahoma City, Okla.).

States have next move in air pollution control . . .

The issuance of air pollution control documents by the Department of Health, Education, and Welfare (HEW) on February 11 triggered the standards setting mechanism authorized by the Air Quality Act of 1967. The four documents include air quality criteria and control technology for sulfur oxides and particulate matter. So, the D.C. Commissioner and the state governors in those air quality control regions that have been designated by HEW each have 90 days to indicate their intent to adopt, implement, and enforce standards for the two specified air pollutants. Then, each will have 180 days to adopt standards, and an additional 180 days to implement plans and enforce the standards. HEW's air quality control regions include the metropolitan areas of New York City, Washington (D.C.), Chicago, Denver, Philadelphia, and Los Angeles. Other regions have been proposed for the metropolitan areas of St. Louis, Boston, Cincinnati, Cleveland, Pittsburgh, Buffalo, and the San Francisco Bay area.

. . . And in Japan, new air quality criteria are imminent

Japan also is in the throes of establishing urban air quality criteria. Last June, Japan's Ministry of Health and Welfare (MHW), which adopted a recommendation lowering to 0.05 p.p.m. the maximum allowable concentration of SO_2 in the atmosphere, now is waiting for agreement by other relevant ministries before the ruling can go into effect. Major holdout has been the Ministry of International Trade and Industry (MITI), which, paradoxically, both represents and regulates the manufacturing industries involved. MHW hopes for MITI approval by March. As in the U.S., the impending regulations are stepping up the competition between SO_2 control techniques, several of which have been under intensive investigation by the Japanese government and industry. Recently, Wellman-Lord, Inc., of Lakeland, Fla., granted a nonexclusive license to two Japanese firms, Mitsubishi Kakoki Kaisha, Ltd., and Sumitomo Chemical Engineering Co., Ltd., for the sale and promotion of Wellman-Lord's SO_2 recovery process (ES&T, November 1968, page 994) in Japan and a number of Asian countries. Both licensees have since discontinued work on their own corporate processes.

Service offers check on research program goals

Science Information Exchange (SIE) services, which include subject searches in current research fields, computer listings, compilations, printouts, catalogs of current research, and other related activities, are now available for a fee to both federal and nonfederal users in research and development areas. Largely restricted previously to federal users, SIE, the Smithsonian Institution's clearinghouse for information on scientific research in progress, is funded by the National Science Foundation and supplemented by funds obtained from service fees. Search of the SIE records—which include 100,000 references to continuing research in the physical, social, and engineering sciences—permits research workers and administrators to avoid unnecessary duplication of procedures in their investigative activities.

The deadliest air pollutants are invisible.

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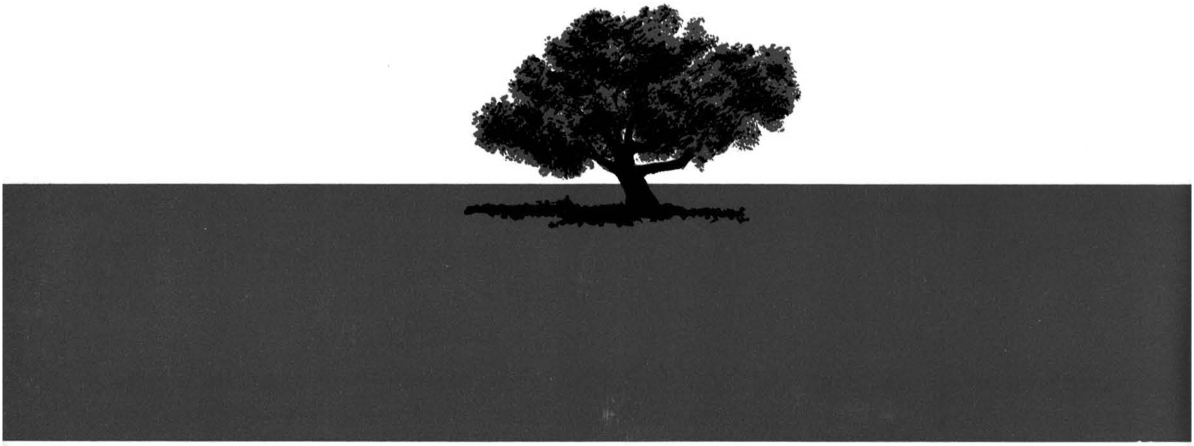

The one sure way to spot the invisible pollutants is to use the right instrumentation. That's where MSA comes in. Whether you're monitoring the atmosphere or checking stack or auto emissions, MSA instrumentation can give your analyzing system its most sensitive "eye."

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The M-S-A Total Hydrocarbon Analyzer uses the hydrogen flame ionization principle for precise, continuous measurement of hydrocarbon concentrations in the atmosphere.

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New legislative proposals for water quality

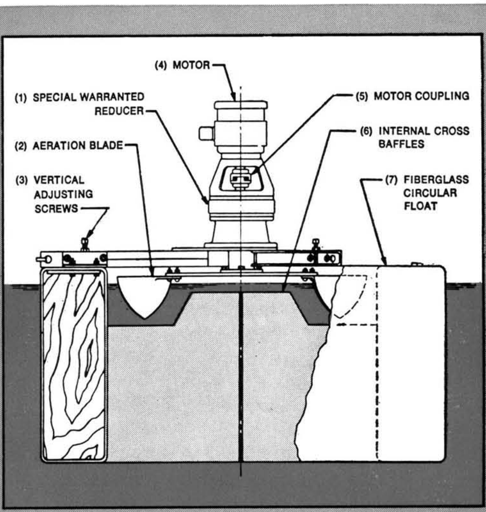
The three remaining uncontrolled major sources of water pollution—oil, sewage discharges from vessels, and thermal degradation of water quality—are the basis for S.7 and S.544, the Water Quality Improvement Act of 1969. Introduced by Sen. Edmund S. Muskie (D.-Me.) and endorsed by 25 other senators, S.7 is basically the same legislation, with the exception of the financing provisions, which the Senate approved unanimously during its last session. Financing provisions are included in Sen. Muskie's S.544. The act calls for: • Cleanup provisions for oil spills and adequate safeguards to prevent the release of oil from onshore and offshore facilities. • Establishment of standards for vessel treatment devices which would prevent the discharge of untreated and inadequately treated sewage from these sources. • Denial of a license or permit by any federal agency for an activity which may affect water quality until it has been determined that the proposed activity will comply with applicable water quality standards. In the past, these licenses and permits were issued without any assurance that the water quality standards would be met or even considered, according to Muskie. Hearings on these proposals begin this month before the Senate Subcommittee on Air and Water Pollution, whose chairman said he hopes Congress will move swiftly on these proposals.

Fight against eutrophication gains momentum

Three recent eutrophication developments—publication of a provisional algal assay procedure, establishment of a new information center, and appointment of a new executive director—were recently revealed by the Joint Industry-Government Task Force on Eutrophication. Theodore E. Brenner, a research director of the Soap and Detergent Assoc., is the new executive director of the joint task force. The development of a standardized test procedure (provisional) to measure the algal growth potential of various chemicals and waters has been achieved and the procedure is available from FWPCA's National Eutrophication Research Program (Corvallis, Ore.). The procedure actually derives from last March's meeting of a group of international experts on the subject. Also, a Eutrophication Information Center (EIC) to provide abstracts, reviews, and reference and library facilities, will be established at a cost of $90,000 at the University of Wisconsin, where EIC will complement Dr. Gerard A. Rohlich's eutrophication research effort.

Air sampler for high altitude developed

A rocket-borne high altitude air sampler developed by scientists at the National Center for Atmospheric Research can collect, at a height of 12 miles, a total volume of more than 10,000 cubic feet (283,000 liters) of air in a 2.3 cubic foot (64 liters) sample chamber for return to earth for measurement and study. When the rocket-borne sampler, known as ENCAR (for **En**closed **C**ryocondenser for **A**ir **R**ecovery), reaches its operating altitude, the sample chamber opens. Movement of the rocket through the air rams air into the sample chamber where the air is frozen out on heat exchanger coils chilled by liquid hydrogen (−423° F.). At completion of sample collection, the sample chamber returns to earth by parachute for analysis for many minor atmospheric constituents, including water vapor, trace gases, and radioactive particles.



(4) MOTOR
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(2) AERATION BLADE
(3) VERTICAL ADJUSTING SCREWS
(5) MOTOR COUPLING
(6) INTERNAL CROSS BAFFLES
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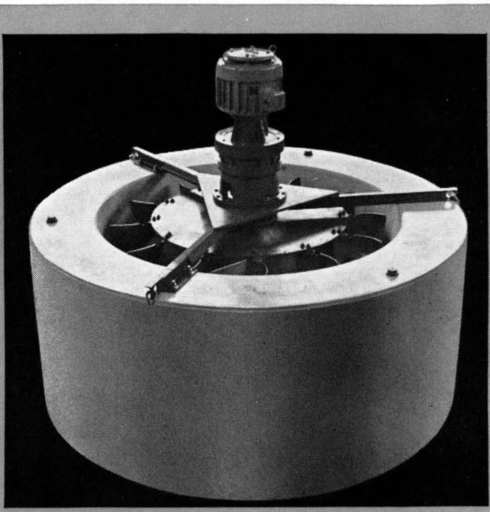


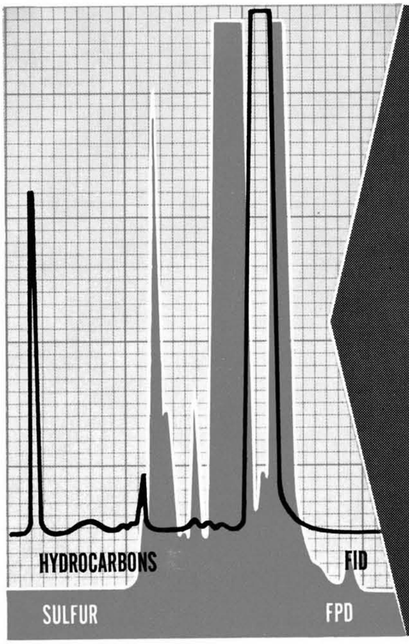
Environmental agencies reorganize

Major reorganizations at several federal environmental agencies have recently occurred. At the **Federal Water Pollution Control Administration** (FWPCA), the reorganization includes: • Reduction in the number of assistant commissioners from seven to four. • Establishment of a new office for program coordination. • Establishment of two new divisions for water quality research and enforcement. At FWPCA, one new position (operations) at the assistant commissioner level was established; three others (research and development, enforcement, and administration) were retained; and four others (facilities programs, technical programs, comprehensive planning and programs, and program plans and development) were abolished. Also abolished: director of the divisions of technical services. Assistant commissioners are: Allan Hirsch, operations; David B. Stephan, research and development; Murray Stein, enforcement; and Edmund J. Grant, administration.

At the **National Air Pollution Control Administration** (NAPCA), Edward F. Tuerk moves up to the post of acting deputy commissioner from the post of special assistant for program operations (ES&T, October 1968, page 727). Three new bureaus—criteria and standards, engineering and physical sciences, and abatement and control—each will be headed by bureau directors who will be charged with the operational responsibility of NAPCA's programs. Bureau directors are Bernard J. Steigerwald (engineering and physical sciences) and Robert L. Harris, Jr. (abatement and control). Other top management posts at NAPCA include: • An associate commissioner for the technical center at Durham, N.C., who will also be charged with the responsibility of the three offices—research grants, manpower development, and technical information and publications. • Four assistant commissioners: John H. Ludwig, science and technology; William H. Megonnell, standards and compliance; Raymond Smith, program development; and Doyle J. Borchers, regional activities. • A new position of assistant to the commissioner for intergovernmental affairs. • Eleven directors—nine for NAPCA's regional offices, one for the office of administration, and one for the office of education and information. Other NAPCA managers are: assistant Jack C. Oppenheimer, intergovernmental affairs; and directors Robert Perman, administration; and Leighton A. Price, education and information. NAPCA, one of three major arms of the Consumer Protection and Environmental Health Service (CPEHS), also gains the air radiological monitoring service.

The **Environmental Control Administration** (ECA), another arm of CPEHS, has reorganized into five bureaus: solid wastes, occupational safety and health, water hygiene, community environmental management, and radiological health. ECA's programs are outgrowths of earlier ones at the National Centers for Radiological Health and for Urban and Industrial Health, both of which have been abolished.

At the **Department of Health, Education, and Welfare,** environmental health sciences rise in stature. A new National Institute of Environmental Health Sciences (NIEHS) has been established, resulting from an outgrowth of the National Institutes of Health's two-year old division (ES&T, October 1968, page 758). NIEHS scientists are working: • To identify harmful environmental agents. • To determine the mechanism by which these agents affect an individual's health. • To develop data on the effects of long-term, low-level exposures.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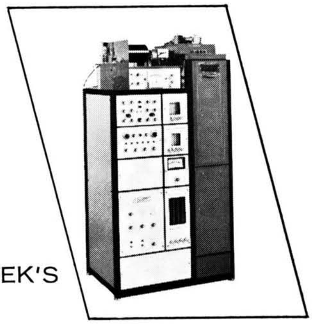


Environmental mutagens society established

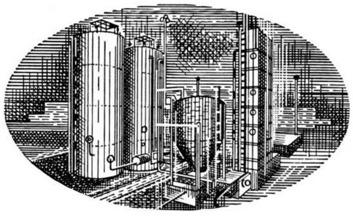
"Concern is now growing . . . that chemical mutagens may pose a potential public health hazard. The identification of potential chemical mutagens that might enter the human environment and the restriction of their use should, therefore, be given high priority." So said Dr. S. S. Epstein, chief, laboratories and environmental toxicology and carcinogenesis, at Children's Cancer Research Foundation, Inc. (Boston), and executive secretary of the newly formed Environmental Mutagenesis Society. Early order of business for the new society is to establish a register of chemicals reported to be mutagenic or nonmutagenic in particular systems. Also, the group plans to prepare a monograph on the state of the art of methods for determining mutagenicity.

FWPCA issues waste heat control guide

"The Industrial Waste Guide on Thermal Pollution," a recent 112-page publication of the Federal Water Pollution Control Administration (FWPCA), aims to provide a practical evaluation of the problems of thermal pollution—and what can be done to control waste heat—according to FWPCA's Commissioner Joe G. Moore, Jr. Developed by the national thermal pollution research staff at FWPCA's Pacific Northwest Water Laboratory (Corvallis, Ore.), the guide will serve as a textbook for two-day seminars that FWPCA plans to conduct at seven locations throughout the U.S. during the first quarter of 1969. The guide includes discussions on industrial waste heat loads; physical, chemical, and biological effects of waste heat; and control of waste heat.

Geologist decries increased use of waste injection wells

Deep-well injection of liquid wastes, far from being a solution to a disposal problem, increases the probability of ground water contamination, according to David M. Evans of the University of Colorado's School of Mines. Evans, who, two years ago, linked the increased frequency of Denver earthquake tremors to the U.S. Army's disposal well at the Rock Mountain Arsenal, warns that increased use of disposal wells (ES&T, June 1968, page 406) is merely a case of "sweeping our pollution problems under another rug." In a paper presented at the Dallas meeting of the American Association for the Advancement of Science, the Colorado geologist discounted the arguments of those who tout the widespread use of oil field brine injection wells as a rationale for promoting underground waste injection. Citing specific examples of brine from such wells affecting surface waters, Evans further reasons that waste wells have a greater chance of leaking than salt water wells. Oil field brine is usually injected into oil- and gas-depleted reservoirs, whereas industrial disposal wells discharge into zones already filled with salt water and raise the reservoir pressure above normal. "It may take decades, or even centuries, but this high pressure will eventually leak out . . . perhaps into other underground zones, perhaps to the surface, perhaps into public waters." Evans' solution: Harmful wastes must never leave the factory, but be reused when possible, stored where available when needed, or cleaned up so that disposal is unnecessary.



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A Monsanto Biodize process offers you maximum capital cost savings because your plant is designed to your specific needs. In fact, construction will be at a fixed cost. Day-to-day operating economics follow as naturally as night follows day. In addition, your plant will handle complete treatment of liquid waste on a piece of land less than half that required for high-rate trickle filters, and less than two-thirds that required for an activated sludge facility.

Our approach involves two basic steps preliminary to plant construction.

First, a preliminary study and laboratory analysis of the actual waste water is made. This determines if the waste is suitable for biological oxidation and establishes the rough range of your needs.

Second, a prototype plant is set up on your site. This step determines your exact requirements, and permits establishment of exact costs. It provides the basis for the plant guarantee.

Result is a pollution control plant that's not under-engineered, not over-engineered—but right on the button.

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Lake Superior: Target for May conference

As one of his last official acts before leaving office last month, Secretary of the Interior Udall took unilateral action by calling an enforcement conference for Lake Superior, world's third largest fresh water lake, and set a precedent for future conferences. None of the governors of Lake Superior's bordering states—Michigan, Wisconsin, and Minnesota—requested the conference. FWPCA's findings of water pollution in Lake Superior are slated for an early spring report that will be the basis for discussion at the enforcement conference scheduled for May.

Canadian-U.S. water standards not met

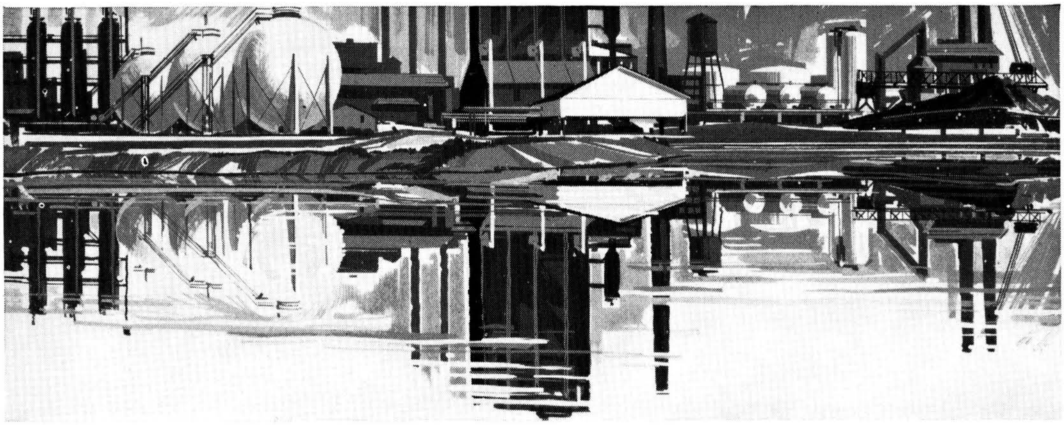
Water quality objectives for international boundary waters in the St. Marys, Detroit, and St. Clair Rivers are not being met, according to findings of an advisory board of the Canadian-U.S. International Joint Commission. At last month's meetings, representatives from industry, federal agencies, and others told the commission of their present abatement efforts and status. Specific objectives were recommended by the commission in 1950 and subsequently approved in the Boundary Water Treaty—an agreement between the two governments that boundary waters would not be polluted in either country to the injury of health or property in the other.

Agriculture becomes pollution abatement target

The Johnson administration left an expensive guide for the incoming Nixon forces in the form of a new Department of Agriculture (USDA) and Office of Science and Technology report, "Control of Agriculture-Related Pollution." Noting that agriculture makes a major contribution to the pollution problem (for detailed discussion see ES&T, July 1968, page 498), the report proposes that agency expenditures for action programs to solve pollution problems related to agricultural activities should average $1 billion each year for the next five years. These expenditures do not include USDA's loan program for such purposes which, the report notes, should increase to $530 million annually from the current $23 million. Proposed expenditures for support of action programs for the five-year period put sediment at $3.8 billion; animal wastes, $900 million; plant nutrients, $253 million; forest and farm crop residues, $174 million; processing wastes, $161 million; pesticides, $92 million; air pollution, $81 million; and inorganic salts and minerals, $25 million.

Udall shifts gears, maintains heading

The environmental crisis cannot be solved, nor can an end be brought to environmental disorder, if specialists in the various aspects of environmental management go about the practice of their disciplines in an uncoordinated way. This generalized restatement reflects the ambitious goals of Overview, the new international consulting firm for a better habitat for man organized by former Secretary of the Interior, Stewart L. Udall. With offices in Washington, D. C., and San Francisco, Overview will seek to implement the founders' belief that total planning—social, economic, political, scientific, and technological—for total environments must be achieved before the evolution of a humane environment becomes a reality. The group's management team will coordinate the selected activities of a collection of principal advisers to meet the immediate problems of people, industry, and governments on a national and international level.



Water...and your P&L Statement

Realistic corporate planning must deal with the unpredictable . . . technological breakthroughs, changes in the tastes and requirements of the market . . . all the imponderables that can change a market picture overnight. Water costs have joined the ranks of the unpredictable.

Published or yet to be published water quality standards may give some indication of how water costs will figure in your future profit statements. These new stream standards must be interpreted, and the possibility of their upward revision must also be considered before adequate planning can be accomplished. Otherwise, you as a corporate planner could find yourself over- or underplanned.

For example, P.R. can be a factor. "Public image" may be no problem for you today, but can become a matter of screaming urgency next year.

And how about the use of municipal facilities for waste water disposal? Such an allegiance may offer economical solutions to pollution problems, but you have to be *sure* that hidden factors or future changes in plant operations do not jump costs out of reason.

And how about plant expansion, your own and that of other plants using the same water source?

So there are problems . . . how about solutions? There is no "stock" answer. Each problem has so many variables that the only way to develop a solution is to define the individual situation. Calgon Corporation has spent a corporate lifetime in learning the skills necessary for just this job.

What is water? A simple chemical which through its very existence, becomes so complicated that a precise definition is very difficult. The chemistry of water has never been emphasized in chemical education, but Calgon engineers and Calgon research have been focused on this specific subject for more than four decades.

The age and size of your plant(s) must be factored in. Very few plants had to consider water as a process problem. The plant was usually built where adequate water was available, and the plant learned to live with whatever water problems developed.

In most plants, water usage and management grew like Topsy, and like Topsy, are not as efficient as could be desired.

A Calgon engineer has the background and experience to determine where water systems can be simplified, where shortcuts and rearrangement can conserve water, cut pollution and save money.

What are the "specs"? Even experienced in-plant water treatment specialists may need help when it comes to applying the new standards to specific plants. To such situations, a Calgon water management specialist brings a wide-ranging background based on experience with many different industrial water problems. He has information on the pollution situation up- and downstream of the plant. He can use his experience to find ways to minimize the plant's total pollution load. In short, he can put all of this and much more together to arrive at the least costly solution.

In effect, you can add an experienced water consultant to your own management staff.

That's why Calgon products and services are used by 98 of the country's largest industrial companies; 47 of the largest utilities and thousands of other plants and municipalities.

The Water Audit™ . . . only sound basis for decision. That's what we have been talking about . . . a really thorough survey of the water management requirements, internal and external, of any plant.

With a Calgon Water Audit, you have in hand a complete analysis of incoming and outgoing water, detailed information on what happens to the water as it goes through the plant, and recommendations on how the systems can be made more efficient. You will *know* how big a waste water problem you have.

Or, the Audit may show that, with the recommended changes, you haven't one at all. If you do need waste water treatment facilities, the Audit will tell you the size and cost of a plant that will meet probable immediate and future water quality standards.

A Calgon Water Audit costs little in comparison to the possible savings, and enables you to budget for future requirements without making an immediate capital investment.

Calgon Corporation water management experts will be glad to discuss the specifics of a Calgon Water Audit with you. For more information, write or phone Calgon Corporation, Calgon Center, Pittsburgh, Pa. 15230. Phone 412—923-2345.

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Oxygen bids for sewage treatment role

Increased plant capacity and lower BOD levels are goals of 19-month field test

Encouraged by the results of pilot tests on the use of oxygen in secondary sewage treatment, Union Carbide's Linde division has begun a large-scale demonstration of the process at the Batavia, N. Y., municipal sewage treatment plant. Armed with a $500,000 grant from the Federal Water Pollution Control Administration (FWPCA), Linde hopes the 19-month test program will confirm a tentative conclusion reached as a result of the pilot test: The use of oxygen in place of air in biological treatment processes can reduce treatment costs by increasing plant capacity, and, at the same time, increase the effectiveness of treatment.

Batavia's sewage treatment plant, which treats an average of 2.5 million gallons per day, uses an activated sludge process for secondary treatment. Linde selected Batavia as a site for the field test because it was one of the few modern activated sludge processes that is equipped for dual train operation. During the test, one of the plant's two separate aeration and clarifier systems will be converted to oxygen aeration; the primary objective of the test will be a detailed comparison of the numerous process variables of the new and conventional systems, operating on the same waste water feed stream.

New and efficient

The essential feature of Linde's oxygenation system is a new, efficient means for contacting the waste water and microorganisms with the oxygen. For, as Linde's Dr. John McWhirter explains, the concept of using oxygen to promote secondary waste treatment is by no means a new idea, and dates back at least 20–30 years. What has thwarted previous efforts at commercializing such oxygenation processes is the low degree of utilization of the oxygen. Oxygen costs at such low efficiencies make the processes economically unattractive.

McWhirter points out that conventional sewage treatment systems are also relatively inefficient in utilizing the oxygen content of the air supplied to the system. Such plants compensate for this inefficiency by using large amounts of excess air. In fact, aeration is usually the largest single operating cost in activated sludge processes.

Pilot. *Mobile laboratory stands a silent watch on pilot operation using oxygen for secondary sewage treatment*

Linde's system of oxygen aeration, on the other hand, allows a higher overall oxidation capacity per unit volume to be attained, to the degree that oxygen aeration now appears economically competitive with conventional aeration.

In addition to the FWPCA study on municipal waste treatment at Batavia, Linde is pursuing its own study on the potential of the process for treating various types of industrial wastes.

Because of patent considerations, Linde does not divulge much detail about the mechanism of its oxygenation system, other than to say that the system is a result of the company's research on high-rate, mass transfer phenomena at gas-liquid interfaces. But a measure of the system's effectiveness can be seen from a study of the results of Linde's pilot tests. Whereas in conventional aeration, the upper limit of dissolved oxygen is 1–2 p.p.m., levels of up to 4–8 p.p.m. can be obtained with the oxygen aeration system. Lower BOD levels in the secondary effluent are also expected as a result of the Batavia tests.

More system benefits

Linde claims other benefits for the system — intense agitation is not required, as in air aeration, with the result that the sludge mass which forms is not dispersed, is readily flocculated, and is more easily removed. The company believes that its system also may improve the means for nutrient removal from secondary effluents. For example, most methods for nitrogen removal depend on biological nitrification of the organic nitrogen, followed by subsequent denitrification to nitrogen gas. Preliminary results indicate that the increased dissolved oxygen level increases the denitrification step, and improves the overall efficiency of nitrogen removal.

New market

Widespread use of the oxygenation process could open up a significant new market for oxygen. Projections based on the total BOD requirements of sewage treatment plants lead McWhirter to speculate that the total potential market could equal or surpass the steel industry consumption of oxygen in basic oxygen furnaces—currently about 200 billion cu. ft. of oxygen per year.

Oxygen demand for BOD furnaces has been responsible for a substantial expansion in total capacity by U. S. producers, with a resultant down-trend in price. A new market of equivalent size would probably reinforce this trend. But McWhirter points out that although small or moderate-sized treatment plants would rely on merchant sources of oxygen, large metropolitan plants might be able to justify on-site oxygen generation.

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Treated watershed yields improved water harvest

Asphalt lining of watershed area competes with other means of enhancing potable water supply

During the spring of 1964, the U.S. Geological Survey began a watershed asphalt-treatment project in an alcove on the edge of mountains near the headquarters area of the White Sands Missile Range. The U.S. Army White Sands Missile Range and the Esso Research & Engineering Co. cooperated in the project. The alcove is bordered on the south and west by the Organ Mountains, on the north by the San Augustin Mountains, and merges with the Tularosa Basin on the east. The project area is about 25 miles east of Las Cruces, N.M., and about 40 miles north of El Paso, Tex.

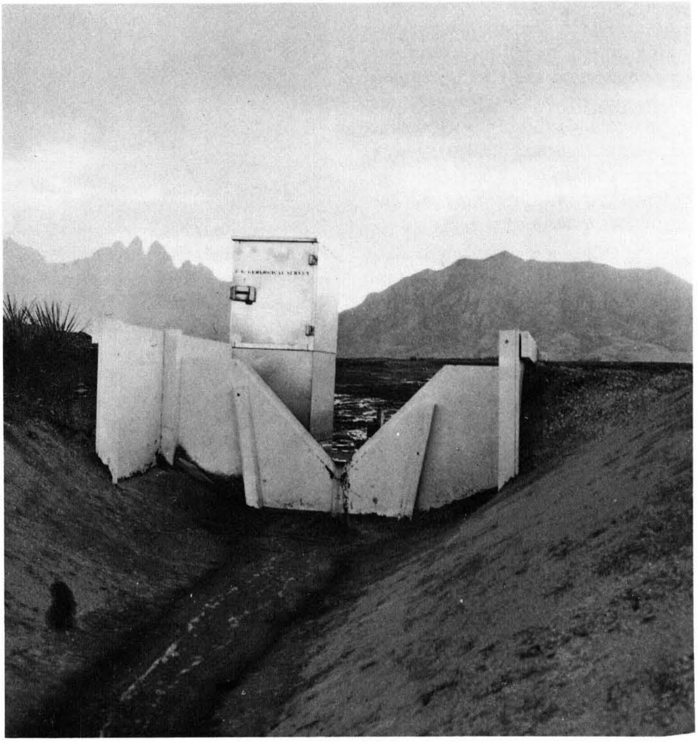
The purpose of the watershed asphalt-treatment project is to determine the increase in surface-water runoff in an arid area caused by applying a thin layer of asphalt on the soil surface of a small watershed. This is an extension of earlier work on a smaller scale by L. Myers (1967). The results will be used to determine the possibility of increasing the supply of potable water to the headquarters of White Sands Missile Range.

Two small, adjacent watersheds of about nine acres each were selected just northwest of the headquarters area. One watershed was cleared of native shrub and covered with a ⅛-inch layer of liquid, commercially available, asphaltic material. The asphalt was applied with RC-250 spray at an average rate of 0.35 gallons per square yard, or 1700 gallons per acre. The other watershed was not disturbed. A recording rain gage was installed in each of the areas to record the precipitation; a V-notch weir was installed in each area to measure the runoff. Recording gages also monitored the height of water and duration of flow at each of the weirs. Infiltration pits were constructed downstream from each of the weirs to collect the runoff, and a recording gage was placed in each pit to record the water level and infiltration rate. This instrumentation provided a means of determining the collection efficiency in the two areas and the amount of water collected which can be attributed to the use of the asphalt coating.

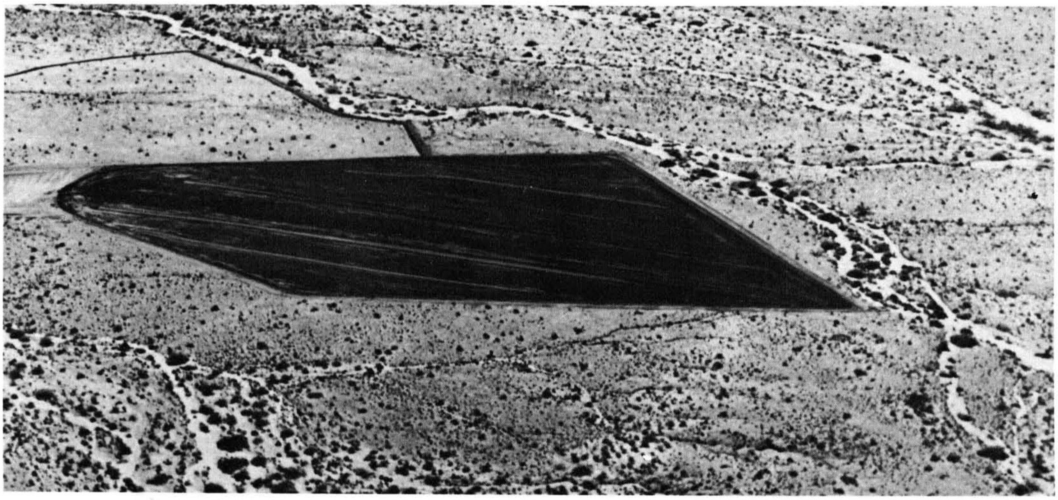
Climate

The White Sands Missile Range area has the arid to semi-arid climate typical of the southwestern U.S. Climatological data have been recorded by the Air Weather Service at the missile range since 1947; the elevation of this station is 4238 feet above sea level. Snow or hail rarely occurs in the project area, and when it does, it is measured (and will be reported in this article) as equivalent rainfall. Average annual rainfall at this station and in the project area is about 10 inches. The rainfall probably ranges from 18–20 inches on the Organ Mountains to the west of the project area, where the land surface rises to more than 7000 feet above sea level.

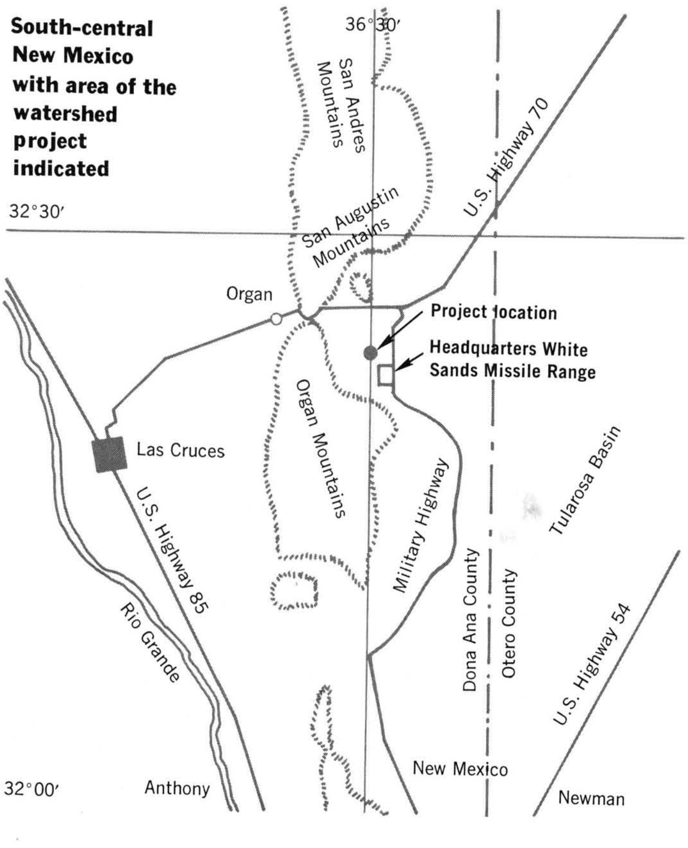
A large part of the rainfall in the area occurs in heavy local showers,



Equipment. *V-notch weir and recorder shelter containing instruments for measuring runoff, height of water, and duration of flow*



Project area. *Aerial view shows the asphalt covered watershed of the White Sands Missile Range*



South-central New Mexico with area of the watershed project indicated

generally in July, August, and September. The relative humidity generally is less than 40%, and, during the summer months, the temperature often rises above 100° F. No weather station reports evaporation rates in the vicinity; however, records from Elephant Butte Dam on the Rio Grande to the northwest, El Paso to the south, and Las Cruces across the Organ Mountains, indicate the potential evaporation from a free-water surface may be as much as 100 inches of water per year.

Analysis

We have concluded an analysis of data collected from May 1964 to May 1966. Part of this record was lost due to instrument malfunction; however, sufficient data were collected to make some determinations on increased collection efficiencies that can be attributed to coating the watershed with asphalt.

The data collected from the untreated watershed indicate a collection efficiency of less than 3%. There were flows through the weir on the untreated area only when the duration of the shower was long and the mean intensity of the shower was very high.

The data collected from the treated area was divided into two parts for analysis. One part contained the data for events when the rainfall was 0.10 inch and above, the other contained data for rainfalls of less than 0.10 inch.

The data from the treated area indicate that a larger percent runoff will occur, for a given amount of precipitation, if the duration of the shower is short rather than long. That is, the efficiency at which an artificial watershed will harvest the rainfall of a particular shower depends not only on the amount of rainfall, but also on the average intensity of the shower.

The amount of rainfall that is retained on the asphalt, as a film held by surface tension, after each shower is constant. The retention constitutes a relatively large fraction of a small quantity of water if the shower is small. Therefore, during a small shower, a previously wetted surface will gain considerably in collection efficiency. Conversely, the influence of rainfall intensity on collection efficiency might be expected to predominate in the case of heavy showers, during which water holdup on the coating would be relatively unimportant. Generally, collection efficiency should be a function of such factors as duration of rainfall, average intensity, ambient temperature, heated surface temperature, and wind velocity. The influence of these factors was also considered in comparing collection efficiencies with inches of rainfall.

Comparisons of runoff in the lower range of rainfall, 0.09 inch precipitation or less, show an initial surface retention loss. Therefore, the collection efficiencies of rainfalls having 0.09 inch precipitation or less rarely exceed 40% and often result in only minute amounts of runoff. For example, on August 28, 1965, a rainfall of 665 cubic feet resulted in collection of only 30 cubic feet, and on February 7, 1965, a rainfall of 1320 cubic feet resulted in a collection of 225 cubic feet.

During heavier rainfalls, the amount of precipitation overcomes the initial evaporation and surface retention losses and, under optimum conditions, exceeds 75% of the rainfall volume.

Cost

The cost to prepare a water harvesting project and the cost per thousand gallons of water delivered depend on the terrain, storage facilities, and the magnitude and duration of precipitation on the area. The preparation of the area prior to the application of the asphalt normally will be a significant part of the cost. However, once the area is prepared, the life of the project could be extended indefinitely by recoating the area when needed.

The cost of preparing the land and applying the asphalt for this project was as follows:

Leveling (bulldozer to clear the brush and level the area)	$ 650
Asphalt (17,600 gallons at 11½ cents per gallon)	2,000
Application of asphalt	2,050
Total cost	$4,700

This resulted in an initial cost of $516.40 per acre. The cost of instrumenting the project is not included.

To maintain the project, it would be necessary to recoat the area with a thin coat of asphalt every 5 years and patch the eroded areas every 2½ years. In order to arrive at the cost of the water collected from the project over a 10-year period, Esso Research & Engineering Co. summarized the initial and repair costs:

Initial cost	$4,700
Maintenance after 2½ years	
Asphalt	200
Application of asphalt	160
5% rise in cost	18
Maintenance after 5 years	
Asphalt	950
Application of asphalt	1,350
Maintenance after 7½ years	
Asphalt	200
Application of asphalt	160
10% rise in cost	36
Total cost for first 10 years	$7,774

During the period from May 1964 through February 1966, about 36 cycles of precipitation and runoff were recorded. The total precipitation amounted to 7.26 inches or 239,600 cubic feet of water on the treated area; the average shower amounted to 0.20 inch. In the same period, 148,771 cubic feet of water passed over the weir, representing a 62% collection efficiency.

The average annual precipitation in the project area is 10 inches. With a collection efficiency of 62%, the project area would collect 6.2 inches of precipitation annually, an amount equivalent to 4.7 acre-feet per year or 15,315,000 gallons over a 10-year period. The project cost for the first ten years is $7,774 and, thus, the cost per 1000 gallons of water recovered would be about 50¾ cents.

Maintenance

The asphalt-treatment project has been installed for about 4 years, and some of the area is in need of repair. Sand from the eroded areas fills the stilling basin and causes the weir stage recorder to indicate less flow than actually occurred. Vegetation has penetrated the thin asphalt coating and cracks appear over a large part of the area. The effect of deterioration of the asphalt coating on collection efficiency has not been determined in our project area. However, such data are available for a similar experimental project conducted in Hawaii.

In a 3-year (1959–61) test of an asphalt-lined catchment area near Holualoa, Hawaii, Chinn (1965) states that the efficiency (ratio of runoff to rainfall) of the asphalt-lined catchment, under minimum maintenance conditions, decreased rapidly with time, from 93% in 1959, to 82% in 1960, and to 78% in 1961. The average for the 3-year period was 84% and rainfall on the catchment averaged 79.2 inches a year during the test period.

The decrease in efficiency was due to:

- Seepage loss through the cracks in the asphaltic membrane as the membrane deteriorated, interception of light rains by the vegetation which penetrated the membrane.
- Interception by depressions in the catchment surface that lost water between storms.

The results of our project thus far indicate that water harvesting from large asphalt-treated areas may be more economical, in some areas, than other means of supplying potable water. For example, about three miles west of the present project area, the annual precipitation is about 15 inches. An area of 5.5 square miles, treated with an impervious material and receiving 15 inches of annual rainfall, would collect 2774 acre-feet of water each year. This amount of water would meet the present water requirements at White Sands Missile Range. Furthermore, this water conceivably could be diverted into a natural underground storage reservoir, such as the cone of depression in the well fields. The result would be a rise of the water surface in the depressed area of the well field, lower costs for pumping the water due to a decrease in lift, less possibility of salt water encroachment, and a more permanent ground water supply.

Federal environmental program budgets show increases for fiscal year 1970

Budget requests for federal environmental programs for fiscal year 1970, which are slightly more than those for fiscal 1969, attest to growing U.S. concern for pollution abatement of water, air, noise, and health hazards. Unlike many other federal programs, the programs for pollution abatement and environmental quality enhancement cut across many federal agencies. The major identifiable and well known programs are those for water pollution abatement in the Department of the Interior and for air pollution abatement in the Department of Health, Education, and Welfare (HEW).

Yet, other lesser known, minor programs include those for noise abatement and an ocean buoy data system in the Department of Transportation (DOT), environmental health sciences in HEW, water resources research in Interior, the International Biological Program (IBP) and the Global Air Research Program (GARP) in the National Science Foundation, and the satellite observation data resources programs in the Departments of Commerce and Interior. All these have increased obligations.

Water

For 1970, the Federal Water Pollution Control Administration (FWPCA) has requested expanded programs for the improvement of water quality. Mainly, these increases include grants to local groups for the development of water pollution control plans for river basins—construction grants will be awarded with federal funding up to 55% of the eligible cost of the project.

This increased effort is expected to result in the evolution of more comprehensive approaches to pollution problems. But the request for FWPCA's direct grant program for the construction of waste treatment facilities remains at last fiscal year's level—$214 million. Still, this request is only a portion of the amount authorized by the 1965 and 1966 Federal Water Pollution Control Acts.

FWPCA has requested no new funds for acid mine drainage field demonstrations. A demonstration program for abating and controlling this form of pollution is in process for mines in the vicinity of Elkins, W.Va. Nor does FWPCA seek any new funds for the construction of water quality standards laboratories. But the request for additional enforcement funds should ensure protection of U.S. water quality and compliance with water quality standards.

Legislation has been proposed which would permit the Federal Government to meet its share for an expanded construction program for a couple of years (see page 101). But the proposals are headed for rough going in the committees of the 91st Congress. Other legislation for control of oil spills, sewage discharge from vessels, and thermal pollution will be rereviewed by Congress.

Interior's Geological Survey has requested increases to accelerate acquisition and dissemination of water data. The Geological Survey's program includes:

- Strengthening basic data collection and analysis.
- Automating the Survey's operations to provide better services.
- Expanding the federal-state program in data-deficient segments of the national water data system.

Air

HEW's fiscal 1970 outlays for research on air pollution and other environmental health hazards will reach $78 million. At the National Air Pollution Control Administration (NAPCA) alone, air pollution abatement and control outlays will increase 13% from fiscal 1969 to $37 million in fiscal 1970. NAPCA's prime target will be the establishment of state standards in 70 air quality control regions. Also in fiscal 1970, NAPCA plans to evaluate several prototype processes to control sulfur oxides emissions.

The number of NAPCA's air pollution grants also are slated for increase. In fiscal 1970, approximately 225 grants for abatement and control will be awarded, compared with 210 in fiscal 1969, and 190 in fiscal 1968. Approximately 350 grants for research, development, and demonstration will be awarded in fiscal 1970, compared with 288 in fiscal 1969, and 236 in fiscal 1968. And approximately 115 grants will be awarded for manpower training in fiscal 1970, compared with 106 in fiscal 1969, and 109 in fiscal 1968.

HEW's Consumer Protection and Environmental Health Service (CPEHS) also supports a national program for the prevention and control of environmental hazards and health problems. As one of three arms of CPEHS, the Environmental Control Administration (ECA) deals with solid wastes disposal, radiation dangers, occupational health hazards, and contamination of water supplies, among others. Part of ECA's budgeted increase will be used for solid wastes field demonstrations, studies in reuse and disposal of wastes, and initiation of computer analysis to solid wastes management. Earlier studies on solid wastes at the Department of the Interior's Bureau of Mines now will be under ECA's purview. ECA's grant activities—nearly 162 grants—remain at the same level as fiscal year 1969.

Weather

Commerce's physical environment program centers on activities at its Environmental Science Services Administration (ESSA). ESSA will use its budget increase for fiscal 1970 for enhancing its program for the dissemination of weather forecasts and warn-

Federal environmental programs

	Federal department and agency	General program	1968 actual	1969 estimate (figures in thousands of dollars)	1970 estimate	Increase or decrease
Air	**Health, Education, and Welfare**					
	CPEHS, NAPCA	Air pollution control	$ 64,174	$ 88,450	$ 95,800	+$ 7,350
	NIH	Environmental health sciences	17,289	18,017	19,004	+ 987
Water	**Interior**					
	FWPCA	Operations and research	92,182	86,550	91,972	+ 5,122
		Construction grants for waste treatment works	203,000	214,000	214,000	—
	OWRR	Salaries and expenses including water resources scientific information center and Geological Survey collection data	11,130	11,181	11,229	+ 48
Solid waste	**Health, Education, and Welfare**					
	CPEHS, ECA	Environmental control, including solid waste	41,736	42,830	57,698	+ 14,868
	Interior					
	Bureau of Mines	Solid waste disposal (Program transferred to ECA)	3,367	317	—	— 317
Pollution forecasts	**Commerce**					
	ESSA	General and special funds: salaries and expenses	107,039	118,458	126,756	+ 8,298
Satellite data	**Interior**					
	Geological Survey	Earth Resources Observation Satellite	—	200	3,800	+ 2,600
Oceans	**Transportation**					
	Coast Guard	Research, development, test, and evaluation, including buoy data system	—	4,000	15,400	+ 11,400
	National Science Foundation	Sea grant program	5,000	6,000	10,000	+ 4,000
Noise	**Transportation**					
	Federal Aviation Administration	Research and development, including aircraft noise and sonic boom problems	27,000	27,000	47,500	+ 20,500
IBP;GARP[a]	**National Science Foundation**	National research programs, including IBP and GARP	15,483	13,000	23,200	+ 10,200

[a] International Biological Program; Global Atmospheric Research Program

Source: Budget of the U. S. Government, Fiscal Year 1970

ings, especially to NAPCA for air pollution forecasts. As part of the U.S. contribution to the World Weather Program, ESSA's research will be directed toward more reliable and longer range weather forecasts on a global basis. Also included in the ESSA budget increase are requests for the purchase of low-level sounding equipment for gathering air pollution data.

In fiscal 1970, ESSA has plans for expanded efforts to develop additional satellite sensors. However, the slight decrease in ESSA's request for satellite funds is due, in large measure, to the longer-than-expected useful life of earlier satellites. Also included in ESSA's plans for fiscal 1970 is the development of the data acquisition system for water resources services.

Lesser programs

The Federal Aviation Administration's Department of Transportation (DOT) program on aircraft safety includes funds for the analysis of aircraft noise and sonic boom problems. The Coast Guard's (also DOT) program calls for funds for an ocean buoy data system.

Increases in the National Science Foundation's (NSF) research program will be used for additional U.S. participation in the International Biological Program. Major integrated research programs will be launched as part of IBP to study biological productivity, human adaptation to changing environment, and the workings of complete ecosystems. NSF's increases will in part go to increased support of the National Sea Grant Program. Such increased support includes a program of grants and contracts, primarily at academic institutions, for developing ways of more effective and efficient exploration of marine resources.

Geological Survey's earth resources observation satellite (EROS) program will continue to receive much attention in fiscal 1970. Indeed, the Survey has requested funds for the EROS program for the following reasons:

- Applications feasibility studies.
- Development of a data management system, including procurement of processing equipment.
- Correlation of satellite acquired data to meet development and management needs of resources programs.

Composite view of U.S. water resources, needs, and problems for next 50 years is good first step

Within the next 50 years, water use in the U.S. will increase drastically. Major U.S. water-using industries—including agriculture, mining, and manufacturing—which withdraw or consume large quantities of water, or add substantially to water pollution, will require greatly increased water supplies. By 2020, major withdrawal uses are expected to increase more than 400% and consumptive uses are expected to more than double. So, changes in technology and efficiency of water use will be a major factor in translating this growth into water requirements.

"The Nation's Water Resources," the first national assessment of U.S. water resources, presents a composite view of water resources problems and requirements for the next 50 years. It describes the U.S. water and related land assets and their use and management problems. This first estimation results from the coordinated effort of many federal, state, and local agencies and private organizations working with the Water Resources Council (WRC), a cabinet-level agency with members from the Departments of Agriculture; Army; Health, Education, and Welfare; Interior; Transportation; Commerce; Housing and Urban Development; and the Federal Power Commission, and observers from the Bureau of the Budget and the Department of Justice.

"The national assessment and the council's framework studies will provide information on water requirements and development potentials that should be of great value to the [newly-established] National Water Commission (ES&T, November 1968, page 991) in its consideration of national policy issues," according to former Interior Secretary Udall, WRC's chairman.

Regions

The council divided U.S. water resources into 20 regions, noting that the first step for each region would be the development of framework plans which would set forth the long-range requirements for each region. Framework studies already are underway in 11 regions, the council notes. The establishment of river basin commissions is yet another goal, and four commissions have been established—the Pacific Northwest, Great Lakes, Souris-Red-Rainy, and New England Commissions—which have developed unified plans and policies for their respective regions. In addition, 49 states now are participating in comprehensive water resources planning, according to WRC.

But the council can foresee certain problems. By 2020, severe water shortages will be common to the Rio Grande, Upper Colorado, Lower Colorado, and Great Basin Regions and to significant portions of the Missouri, Arkansas-White-Red, Texas-Gulf, and California Regions. In addition, severe water quality problems resulting from high degrees of use and reuse will be common to the Great Lakes, Ohio, and Upper Mississippi Regions and significant portions of the North Atlantic and South Atlantic Regions, according to the council.

The council's evaluation—which was recently submitted to the Congress—as well as the council itself, were authorized by the Water Resources Planning Act of 1965 (P. L. 89-80). The assessment is based on 1965 data on water use, with limited analysis, and certain assumptions, including a 1.6% projected increase in population growth and a conservative 4.0% projected

Summary of existing and emerging regional water management problems

	Adequacy of annual natural runoff[a]	Ground-water storage depletion[b]	Water quality				Flood damages[g]	Watershed lands[h]	Beach, shore, and riverbank erosion[i]	Wetlands[j]
			Wastes[c]	Heat[d]	Salinity[e]	Sediment[f]				
North Atlantic	■	■	✱	✱	●	■	■	■	▲	▲
South Atlantic-Gulf	●	■	▲	■	●	▲	▲	▲	✱	✱
Great Lakes	■	●	✱	✱	●	■	●	●	■	■
Ohio	■	●	▲	▲	●	■	▲	■	●	●
Tennessee	●	●	■	■	●	■	■	■	●	●
Upper Mississippi	■	●	▲	▲	●	■	▲	■	▲	▲
Lower Mississippi	●	●	■	●	●	✱	▲	▲	▲	▲
Souris-Red-Rainy	▲	●	■	●	■	●	▲	●	■	▲
Missouri	▲	▲	■	■	■	▲	✱	▲	▲	▲
Arkansas-White-Red	▲	✱	■	●	✱	▲	▲	▲	✱	▲
Texas-Gulf	▲	✱	▲	■	▲	▲	■	▲	▲	▲
Rio Grande	✱	✱	▲	●	✱	✱	■	▲	■	●
Upper Colorado	✱	●	■	●	■	▲	●	■	●	●
Lower Colorado	✱	✱	▲	●	✱	✱	■	▲	■	●
Great Basin	✱	■	▲	●	■	■	●	■	●	■
Columbia-North Pacific	■	■	■	▲	●	●	▲	■	■	▲
California	▲	▲	▲	■	▲	■	▲	▲	▲	■
Alaska	●	●	■	●	●	●	■	●	▲	■
Hawaii	●	■	■	●	●	●	●	■	▲	●
Puerto Rico	●	●	■	●	●	▲	●	▲	■	●

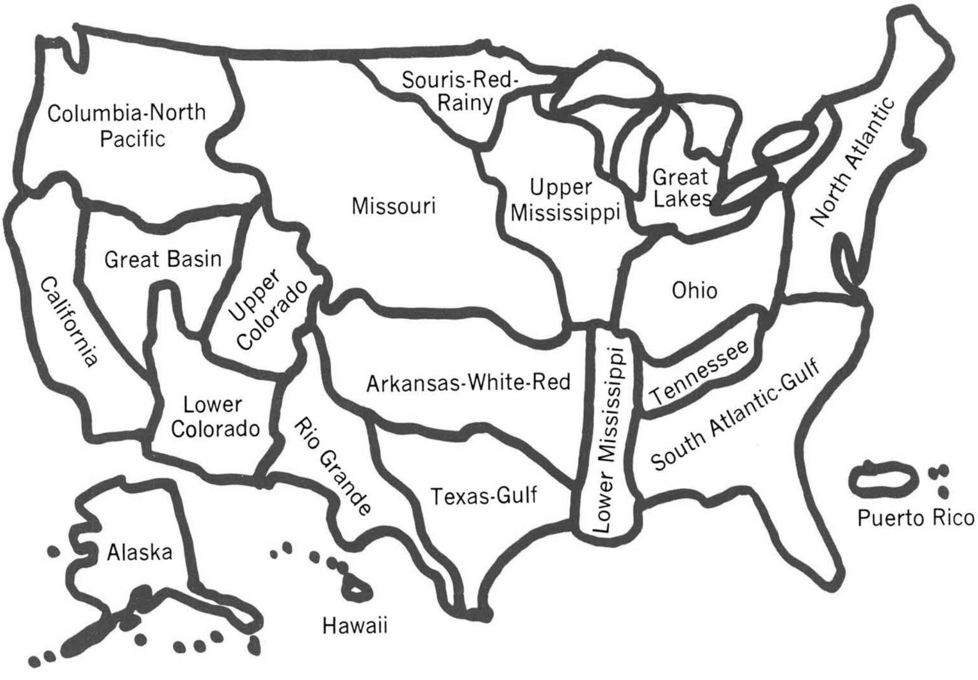
● Minor problem in some areas

■ Moderate problem in some areas or minor problem in many areas

▲ Major problem in some areas or moderate problem in many areas

✱ Severe problem in some areas or major problem in many areas

Water resources regions used in the first national assessment



First step. *U.S. water resources are divided into 20 regions, prior to the establishment of river basin commissions*

annual growth for the gross national product to $4,686 billion (1954 dollars) in 2020. The council recognizes that this first report relies heavily on the judgement of federal and state water officials. But WRC maintains a continuing study of the adequacy of water and related land resources to meet the requirements in each water resource region.

Water uses

The WRC assessment divides water uses into two categories—withdrawal uses that remove water from its natural course and instream uses that do not. Some uses of water, such as hydroelectric power and recreation, may fall into both categories; however, owing to insufficient the report was unable to consider these refinements.

Withdrawal uses primarily are applied to domestic and municipal, industrial, steam-electric power, and agricultural purposes. The increase in domestic and municipal withdrawals relate principally to population increase, according to WRC's findings. Industrial water uses are dependent upon technological advances. In manufacturing, for example, recirculation within the plant is expected to increase from an average of 2.3 times intake in 1965 to 6.3 times intake in 2020. In steam-electric power production, the increased use of cooling towers and other recirculating processes is expected to increase the ratio of water for condensing requirements for fresh water withdrawals from 1.2 in 1965 to 1.9 in 2020.

But the first assessment is not without its limitations. Data on the use of water resources are quite inadequate, according to the council's consensus. These inadequacies place a severe limitation on comprehensive planning, this assessment itself, and other activities requiring inventories of water use. Lack of comparable data on instream uses prevented the comparison of water requirements for instream use with potential flows. Nevertheless, limited analyses of the instream use for hydroelectric power, navigation, recreation, and fish and wildlife uses were included in the evaluation. By 2020, the total hydroelectric capacity will grow more than fourfold, and waterborne navigation will increase sixfold, according to WRC's projections. But the translation of these requirements into water requirements is beyond the capability of the first assessment and will have to wait until future investigations, according to WRC's findings.

Summaries of water resources problems for each of the 20 regions were prepared by field groups of federal and state water experts. These summaries account for half of WRC's 472-page assessment and cover the following items:

- Description of region.
- The water resource.
- Present water resource development–1965.
- Adequacy of present development.
- Present institutional and management problems.
- Projected regional economy and water requirements.
- Emerging water problems.
- Development and management needs–1980.

Future national assessments will lead to a comprehensive framework planning program, computer simulation of the national program, and, ultimately, analyses of tradeoffs between various uses of water.

Study group asks for new marine science agency

Julius A. Stratton, *Marine Science Commission's chairman*

The report of the Commission on Marine Sciences, Engineering, and Resources, a two-year study put in motion by the Marine Resources and Engineering Development Act of 1966, crossed the desks of the incoming and outgoing Presidents shortly before the inauguration. That the issuance of the report was overshadowed by other matters that usually dominate the interregnum—inauguration day plans, confirmation of cabinet members, and maneuvering for congressional leadership posts—is somewhat ironic. Many of the study's recommendations will be pondered and discussed long after the inaugural parade grandstands have been dismantled and cabinet members and congressional leaders installed.

The basic objective of the 15-member commission was the development of a plan for reorganization of the badly splintered federal marine sciences and oceanographic effort; this it does, in a grand, if somewhat predictable, style. These programs, the commission recommends, should be guided by a new, top-level civilian agency, reporting directly to the President: a National Oceanographic and Atmospheric Agency (NOAA). This agency would absorb a large share of the nonmilitary marine programs scattered among various federal agencies and departments. Initially, NOAA would assimilate the U.S. Coast Guard from the two-year old Department of Transportation; the Environmental Science Services Administration and the Bureau of Commercial Fisheries from the Department of Commerce; the Sea Grant Program from the National Science Foundation; the Great Lakes Survey activities of the U.S. Army Corps of Engineers; and the National Oceanographic Data Center. Advising NOAA would be a National Advisory Committee for the Oceans (NACO), comprising about 15 extragovernmental representatives of U.S. marine and atmospheric interests.

More than just an agency

But the commission's recommendations go far beyond the establishment of a top-level oceanographic agency. Viewing the ocean's economic potential as one justification for a strong marine program, the commission devotes one third of the massive report's recommendations—there are about 125 of them—to building up the technological, legal, and international framework for developing the living and nonliving resources of the sea. Surveying and control of the global environment is another major area of the report's concern.

Most of this work would be done through NOAA. But there is a mixed bag of suggestions for a variety of other federal agencies, agencies as diverse as the Federal Power Commission (reexamine differential price policies for natural gas to reflect cost of offshore production), the Department of Health, Education, and Welfare (to establish a National Institute of Marine Medicine and Pharmacology), and the Department of Transportation (initiate an intensive study of the nation's ports and waterways). Not surprisingly, then, in view of the scope of the report, many of its recommendations relate directly to pollution abatement and environmental management.

Antipollution recommendations

The problems of pollution, in fact, "have taken a prominent role in the commission's studies and recommendations," the report notes. The commission concedes that pollution and waste disposal in the oceans and estuaries are often inseparable from pollution upstream—including even the land environments—and must be treated as a single problem.

Thus, some of the commission's recommendations on pollution are broad, perhaps necessarily so: a national commission to study and deal with the total waste management problem; and increased emphasis by the Federal Water Pollution Control Administration on research into identification of specific pollutants and their effects.

But in at least two areas, the coastal zone and the Great Lakes, the commission met pollution problems head on and projected specific programs.

The states must be the focus for responsibility and action in the coastal zone, in the commission's view.

Cost of commission's recommendations

Activity	Average annual cost 1971-75	1976-80	Ten-year total costs
	(millions of dollars)		
Management and operations	62	70	660
Research and education	142	226	1,840
Specific technology	124	182	1,530
Fundamental technology	130	210	1,700
Mapping, charting, and surveying	34	45	395
National projects:			
Test facilities and ranges	43	57	500
Lake restoration	15	20	175
Continental shelf laboratories	40	60	500
Continental shelf nuclear plant	20	26	230
20,000-foot exploration submersibles	20	37	285
Pilot buoy network	15	2	85
Feasibility studies of future projects	7	13	100
All recommendations	**$652**	**$948**	**$8,000**

Nevertheless, the states lack adequate machinery for the task. The report, therefore, recommends that a coastal management act be enacted to provide policy objectives, and to authorize federal grants-in-aid to facilitate the establishment of state coastal zone authorities. The key function of these authorities would be to manage the coastal waters and adjacent land, and to regulate and develop these areas. The authorities would be given the power and funds to acquire these lands when public ownership is necessary to control their use. The Federal Government would meet one half of the operating costs of the authority for the first two years, but would not impose any particular form or organization on the state authorities. Approval of the grants, to be administered by NOAA, would be contingent only on demonstrating that the proposed state organization has the necessary powers to accomplish its purpose.

Coastal zone problems

The commission also studied some of the specific problems related to coastal zone management. It recommends, for example, that AEC be given the power to consider the environmental effects of projects under its licensing authority. AEC, supported by the Justice Department, has held that it lacks authority to consider the effects of thermal pollution in granting power plant permits.

Similarily, the commission would amend the Rivers and Harbors Act to specifically empower the U.S. Army Corps of Engineers to deny a permit for harbor construction activity when such activity interferes with recreation, conservation, or upsets aesthetic values. The act now requires the Corps to consider "all relevant factors . . . including pollution and the general public interest." But the statutory authority to deny permits for reasons other than obstruction to navigation is uncertain and should be clarified.

Setting national projects

A more far-reaching recommendation in the context of coastal zone management is that NOAA undertake one of several national projects envisioned for NOAA by the commission—fundamental engineering and feasibility studies relevant to the development of offshore terminals, storage facilities, and nuclear power plants. Offshore and underwater cargo facilities may provide alternatives to expensive dredging of channels for deep draft vessels; underwater nuclear power facilities should be investigated with the aim of reducing the possibilities of accident, avoiding excessive heating of coastal water, and enriching coastal waters by creating upwelling of nutrients.

Another of the national projects the commission proposes is the restoration of the Great Lakes. The commission's Subpanel on Marine Engineering and Technology developed the concept of a fresh water lake restoration project to be pursued as a feasibility test on a lake of manageable size.

Research into the ecology of the lake selected would be followed by technological development of pollution measuring devices; inflow and outflow design and control; aeration techniques; large-scale mixing techniques; thermal pollution control; artificial destratification; thermal upwelling techniques; filtering; mass harvesting of plants and animals; restocking; and ecological manipulation. The commission recommends that once the restoration technique has been shown to be feasible, FWPCA would assume responsibility for its implementation on one of the Great Lakes.

Big program, big funds

The commission estimates that implementation of its program for coastal zone management would require federal expenditures in this area to increase steadily to $120 million per year by 1980. Total 10-year cost for coastal zone management, including $175 million for the feasibility study for the Great Lakes restoration project, would be $1 billion compared with a 10-year cost for all the commission's recommendations of $8 billion. The commission's program is "not a crash endeavor, but one geared realistically to the means of the nation," in the words of the report.

Marine science has become big science, the commission also points out, and the report designs an elaborate superstructure for its conduct. NOAA's main research arm would be the 38 federal laboratories, suitably strengthened and consolidated, of the various agencies from which it was formed.

In addition, NOAA would support a small group of laboratories selected from the present leaders in marine science, and designated as university-national laboratories. These laboratories would be equipped to undertake marine projects of a global or regional nature. Creation of such laboratories, the commission urges, would be cheaper than attacking major projects on a facility-by-facility basis. In addition to NOAA support, the university-national laboratories would seek funds from other groups, such as the National Science Foundation and the Office of Naval Research, which presently are the two major sources of ocean research support. A third level of laboratory support would be available in university-affiliated coastal zone laboratories, established within the proposed coastal zone authorities.

No wet NASA

In spite of the parallelism between the NOAA-NACO structure and that of the National Aeronautics and Space Administration (NASA)-National Advisory Committee on Aeronautics, Dr. Julius Stratton, the commission chairman, disdains use of the epithet "wet NASA" in describing NOAA and its mission. The ocean program differs from the space program in timing, level of financing and technology development required, and economic return involved. However, the commission seems to have learned something from NASA's early promoters; two immediate goals suggested for NOAA are strongly reminiscent of the manned lunar landing committment:

- Development of the necessary technology to make possible production work for sustained periods at depths down to 2000 feet.
- Development of a technical capability to explore the ocean depths to 20,000 feet within a decade and to utilize the ocean depths to 20,000 feet—which comprises 98% of the ocean floor—by the year 2000.

The report would seem to provide heady stuff for the incoming administration. Some action will be necessary soon to fill the gap in marine science management which now exists. The commission, whose raison d'etre was the report, ceases to exist 30 days after the report is filed. Furthermore, the Council on Marine Resources and Engineering Development, also created by the Marine Resources Act to provide interim planning and coordination of marine affairs, is scheduled to expire June 30. The commission has asked, however, that the life of the council be extended until such time as the full recommendations of the commission are acted upon.

Scrap tires: materials and energy source

Coking oven tests demonstrate feasibility of extracting hydrocarbons from discarded tires

Worn-out tires—approximately 100 million of which are discarded in a haphazard manner each year—may one day become a secondary source of energy and chemical raw materials while losing their status as an environmental disposal problem. That's the hope of scientists and engineers at Firestone Tire & Rubber Co. and the U.S. Bureau of Mines Coal Carbonization Laboratory, Pittsburgh, Pa.

By subjecting shredded used tires to essentially the same process used in coking of coal for the steel industry, these workers have demonstrated the feasibility of extracting various chemicals, liquid oils, gas, and tars from the tires. According to pilot plant operational data, the technique is capable of recovering 40-60% of the tire materials, in a gas or liquid form, from a product which presents, at best, a troublesome solid waste disposal problem.

The question of scrap tire disposal has been broached off and on for some time in discussions within and between government agencies such as the Departments of Commerce and Health, Education, and Welfare, as well as in the rubber industry itself. Most discussion has ended on the note that scrap tires, though perhaps not yet as serious a disposal problem as other facets of the solid waste crisis, could become grounds for serious concern if present consumer trends and disposal practices continue.

Peripheral solutions

The Firestone-Bureau of Mines work is probably the first effort to add a new dimension to past peripheral solutions—for example, the use of shredded tires in rubberized pavements (synthetic latex is cheaper), or as landfill, or as compost material (for which scrap tires aren't well suited).

Firestone's interest in the project, in particular, is another manifestation of what is, perhaps, a trend: More and more manufacturers are extending their concern for their product beyond its normal service life, and are studying the impact of disposal of the product on technology of solid waste.

Firestone, which developed a proposal to reclaim valuable constituents from scrap tires, approached the bureau with the plan because the bureau had facilities well-suited to the project's goal. The bureau's experimental unit at its Pittsburgh laboratories includes extensive instrumentation for collection and identification of the process byproducts. Through a cooperative agreement, Firestone supplied funds for the project and part of the technical personnel. Initial results from the project show that by heating at 500° C. in the absence of air, a ton of scrap material can be made to yield:

- As much as 140 gallons of liquid oils, similar in composition to conventional coal chemicals.
- 1500 cu. ft. of gas, equivalent in heating value to natural gas.
- A solid residue of friable, high-carbon-content material.

The project is in keeping with most modern thinking about our solid waste crisis, which stresses reclamation and upgrading the value of waste materials as the ultimate solution. In the case of used tires, reclamation is unusually attractive since after their expected service life, they retain up to 80% of the total manufacturing value that has been added. Yet, because of the circumstances which govern a resource-rich economy such as that of the U.S., less than a quarter of the tires removed from use are reconditioned by recapping. This low re-use figure is in marked contrast to the recapping rate of some other countries, where the figure runs as high as 80%. In the U.S., the remainder of the tires—save those that see use as tugboat bumpers, backyard swings, or in improving the running ability of football players—persists as a perennial problem for tire dealers, service stations, and ultimately, municipal refuse agencies.

Reclamation also makes sense after consideration of the fact that scrap tires are not suitable for disposal by conventional means. Municipalities that use incineration usually will not collect discarded tires, because refuse incinerators are not designed to burn rubber efficiently. The melted rubber drips through the grates, or forms a compact mass that does not burn completely. Those that are burned in open dumps, usually illegally, under low temperature conditions, with a plentiful supply of cool air, form dense clouds of black smoke and unburned hydrocarbons. As a result, most discarded tires eventually find their way to landfill sites, although tires are far from ideal fill material.

Clean burning

Scrap tires do have a heating value higher than most coals, and the possibility of power generation in incinerators designed for clean burning of bulk tire quantities is being actively pursued in England. But this approach has drawbacks: Design of such incinerators will require considerable development effort, and, also, there are air pollution problems. The sulfur content of rubber often exceeds that of high sulfur coal, and such incinerators would require, therefore, extensive SO_2 control equipment.

Some scrap rubber, predominately from tires, at present is reclaimed in solid form and used in the production of rubber goods. Although most major rubber companies use some reclaimed material, in a variety of products, only a handful of U.S. companies specialize in reclaimed rubber processing. But the total amount used is small—about 250,000 tons per year—and has declined to about 10% of new rubber production at present, compared with 30% in 1945. One reason for this decline is that collection, transportation, and reprocessing costs often exceed new production costs of the cheaper synthetics. Another cause is increasing use of oil-extended rubber.

Thus, increased use of reclaimed rubber as a means of alleviating a solid waste problem would depend on upgrading the value of the recovered material. The Firestone-Bureau of Mines approach, though as yet a long way from this goal, appears to be a substantial step in that direction.

Approval of standards sets pace for protection of U.S. water quality

Today's standards are the law of the land

The water quality standards program, the first systematic nationwide strategy for water quality management, offers a blueprint for victory over water pollution in the U.S. "Progress made in the program has been very encouraging," said Secretary of the Interior, Stewart L. Udall, at his farewell press conference last month. But adequate provision for financing the construction of waste treatment plants is one of the most important items that Udall leaves to the new administration. "The water pollution control program is not going to move forward at the rate that it must, if we are going to roll back pollution, unless the Federal Government figures out a way to get its money on the line," says the departing secretary.

As Udall leaves the stewardship of U.S. conservation and water pollution interests to his successor, water quality standards for 51 (of a total of 54) jurisdictions (47 states plus 4 others) for their interstate and coastal waters have been approved. Of the 47 state standards, 26 have been approved, with certain exceptions for temperature, dissolved oxygen, and certain other criteria. Twenty states have adopted nondegradation statements.

As of January 20, water quality standards were unapproved for three states—Kentucky, Kansas, and Iowa. In the cases of Kentucky and Kansas, Max N. Edwards, Interior's assistant secretary for water quality and research, sent letters to Ralph Pickard, executive director of the Kentucky Water Pollution Control Commission, and to Governor Robert B. Docking of Kansas, commending each of them for working out certain revisions in their standards which are necessary for approval. When the two states ratify these revisions, their standards will be acceptable to the department.

Iowa is the remaining state whose water quality standard is unapproved. It is the only state for which a meeting of the minds has not been achieved. But to reach a final decision on all water quality standards before leaving office last month, Udall set a precedent by calling the first U.S. federal standards setting conference. In Interior's letter to Governor Robert D. Ray, Udall approved Kansas' standard for interstate waters other than those of the Mississippi and Missouri Rivers, informing him that one portion of the conference—for interstate waters of the Mississippi River—will be held on April 8 and a second portion of the conference—for interstate waters of the Missouri River—will be held on April 15. Murray Stein, assistant commissioner for enforcement at the Federal Water Pollution Control Administration, will preside at the conference.

"Water quality standards are the most significant developments that have occurred in the water resources field in recent years," says Robert S. Burd, FWPCA's acting deputy assistant commissioner for operations, who, prior to his recent promotion, directed the water quality standards program since its inception 2½ years ago. In a recent interview, Burd elaborated on the program and targeted additional refinements in standards.

Development

Each standard comprises three essential elements—specification of water uses, establishment of criteria to protect these uses, and an implementation plan. During the past three years, the standards topped the list of priority items of every state's water resources agency. "They are what the whole business of water quality is all about," says Burd.

For the first time, the public and state and federal officials have each had an opportunity to participate in the development of standards. But the process toward clean water will not stop with approval of the last jurisdiction. FWPCA looks forward to more refinements in these standards, as new data become available.

Burd admits that states had a relatively short period of time to develop and submit standards; lack of information on individual states' water quality was surprising. Data on the conditions of each state's waters simply were not detailed nor were they very abundant.

"We have to admit that agreement has not been reached for Iowa's standards," says Burd, indicating that this lack of agreement between federal and state officials centers on the need for secondary treatment for significant and industrial municipal discharges to

54 Water quality standards jurisdictions[a]

	Standard approved	Acceptable nondegradation language	Exceptions[b]		
			Temperature	Dissolved oxygen	Other
Alabama	✓	✗	✓	✓	✗
Alaska	✓	✗	✗	✗	✓
Arizona	✓	✓	✗	✗	✗
Arkansas	✓	✗	✗	✗	✗
California	✓	✓	✓	✓	✗
Colorado	✓	✗	✓	✓	✗
Connecticut	✓	✗	✗	✓	✗
Delaware	✓	✗	✗	✓	✓
District of Columbia	✓	✗	✗	✗	✗
Florida	✓	✓	✗	✗	✗
Georgia	✓	✗	✗	✗	✗
Guam	✓	✓	✗	✗	✗
Hawaii	✓	✗	✗	✗	✗
Idaho	✓	✗	✗	✗	✗
Illinois	✓	✓	✓	✓	✓
Indiana	✓	✗	✗	✗	✗
Iowa	✗	—	—	—	—
Kansas	✗	—	—	—	—
Kentucky	✗	—	—	—	—
Louisiana	✓	✗	✗	✓	✗
Maine	✓	✗	✓	✓	✓
Maryland	✓	✗	✗	✗	✗
Massachusetts	✓	✗	✗	✗	✗
Michigan	✓	✓	✓	✗	✗
Minnesota	✓	✗	✓	✓	✓
Mississippi	✓	✗	✓	✓	✗
Missouri	✓	✓	✗	✓	✗
Montana	✓	✓	✗	✗	✗
Nebraska	✓	✓	✗	✗	✗
Nevada	✓	✓	✗	✗	✗
New Hampshire	✓	✓	✓	✗	✓
New Jersey	✓	✓	✓	✓	✗
New Mexico	✓	✓	✓	✓	✗
New York	✓	✗	✗	✗	✗
North Carolina	✓	✗	✓	✓	✗
North Dakota	✓	✗	✗	✗	✓
Ohio	✓	✓	✓	✓	✓
Oklahoma	✓	✗	✗	✓	✗
Oregon	✓	✓	✗	✗	✗
Pennsylvania	✓	✗	✗	✗	✗
Puerto Rico	✓	✓	✗	✗	✗
Rhode Island	✓	✗	✗	✓	✓
South Carolina	✓	✗	✓	✓	✗
South Dakota	✓	✗	✗	✗	✗
Tennessee	✓	✗	✓	✗	✗
Texas	✓	✗	✗	✗	✗
Utah	✓	✓	✗	✗	✗
Vermont	✓	✗	✓	✓	✓
Virginia	✓	✗	✓	✓	✓
Virgin Islands	✓	✗	✗	✗	✗
Washington	✓	✓	✗	✗	✗
West Virginia	✓	✗	✗	✗	✓
Wisconsin	✓	✓	✗	✗	✗
Wyoming	✓	✓	✗	✗	✗
Totals	51	20		26[c]	

Yes ✓ No ✗

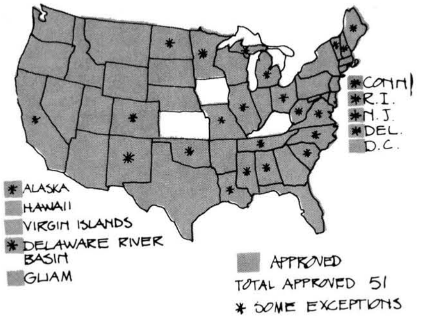
[a] exclusive of Delaware River Basin Commission [b] as of January 20, 1969 [c] total for three columns

Source: Federal Water Pollution Control Administration

the Missouri and Mississippi Rivers. But federal standards may be imposed on some state's interstate waters such as Iowa's. Failing to reach agreement in discussions with Iowa's former governor, Harold Hughes, Udall noted that Interior has no choice now but to set federal standards. Interior asks only that Iowa require the same degree of treatment as that specified by its neighboring states whose water quality standards have been approved. But Iowa's officials remain adamant on the issue.

The approval procedure for standards was slowed down in many cases by a state's administrative procedures. After federal and state water pollution control officials agreed in principle on a particular course of action, individual states had to seek formal ratifications. "Required by law, these ratifications, in some cases, consumed considerable time," Burd explains. Frequently, this process called for the scheduling and holding of public hearings or action by the state water pollution control board. Normally, these procedures required 30 days notice of the public hearing and another 30 days for keeping the official record open after the hearing. "Each state applies its own administrative procedures, and obviously, different time schedules are involved for each state," Burd notes.

FWPCA commissioner Joe G. Moore, Jr., visited all regional FWPCA offices and met with state administrators and federal officials from each



Approvals. *Federal water quality standards—with some exceptions—for nearly all U.S. interstate and coastal waters now are in effect. Developed jointly by federal and state officials, the standards offer a guide for future protection of U.S. waters*

region in an attempt to obtain clearer understanding on water quality standards issues and to discuss other programs of mutual interest.

Now, approximately half of the states have proposed nondegradation language acceptable to the Secretary of the Interior. "By mid-year, all states will have acceptable nondegradation language in their water quality standards," Burd says wistfully.

During the past one and one half years, guidelines slowly have evolved in the review of standards. "We have taken another look at the original 10 states' standards submissions which were approved to assure that a consistent course of action is taken by the department," he explains. "We expect, where appropriate, that some portions of these . . . will be revised to bring them more closely into line with later approvals."

Secondary treatment

Secondary treatment of all significant municipal and industrial wastes for discharge to fresh waters is a FWPCA goal. Most states initially specified a minimum of secondary treatment for all wastes, in recognition that this feasible level of treatment was necessary to meet state and federal objectives to enhance polluted waters and protect existing quality of unpolluted waters. Other state standards do not require a flat commitment to secondary treatment of all wastes. Burd notes that a few coastal states having ocean outfalls—such as Washington, California, and Massachussetts—specify primary treatment. For example, Massachusetts' standards were approved with only primary treatment required for Boston. "However, if technical studies indicate some detrimental effect in Boston's water quality, then we and the state may find that secondary treatment will be required," Burd intones. "FWPCA and the state have such a study underway today. The study aims to find the effect of primary treated wastes, which are discharged to the ocean, on Massachusetts' water quality. If the study concludes that primary treatment is not adequate, then we may have to go back at a later date and require secondary treatment of Boston's wastes," explains FWPCA's spokesman.

FWPCA will continue to stress its view that secondary treatment should be the minimum goal for significant wastes discharged to fresh waters, in order to comply with the intent of the Federal Water Pollution Control Acts. Burd explains that FWPCA thinks the treatment requirements for insignificant wastes and wastes discharged to the open ocean should be evaluated on a case-by-case basis. "A change in this policy recommendation on standards is not likely to occur," Burd reassures. The treatment issue had to be resolved because the implementation plan, the third element of every water quality standards package, is an important item on which federal and state officials must find a meeting of the minds.

Regional differences

Some eastern states—such as New York, Connecticut, Massachusetts, and New Jersey—have issued literally hundreds of orders to comply with the secondary treatment requirement for municipal wastes and equivalent treatment requirement for industrial wastes. But a comprehensive evaluation of the status of compliance with state standards is premature at this time. Typical compliance dates target 1972, but there is nothing magic about that year; a few dates are earlier, and others are later. Originally, the compliance date generally was set at five years after the submission of standards, which were adopted by each state before June 30, 1967. State officials felt there was sufficient time, within the five-year period, to design, arrange financing, and build the requisite treatment facilities, according to the FWPCA spokesman.

"In the western states, you often hear of a conflict between water quality and existing patterns of water rights," says Burd. "Local institutions are reluctant to use stored waters for dilution of wastes. These groups feel that any water accumulated in reservoirs could be better used for irrigation or public and industrial water supply."

But Burd clarifies the situation by emphasizing that western states have a good record for prescribing a high level of waste treatment—for example, the Pacific Northwest Pollution Control Council, an interagency group, established and adopted water quality objectives as early as 1952. "Dilution of wastes by stored waters hasn't been considered a satisfactory alternative to waste treatment," Burd adds.

Industrial differences

Wastes from industries vary. Some are organic, others are inorganic; some are amenable to biological treatment, others are amenable to chemical treatment. For example, today, the organic wastes from the food processing and pulp and paper industries can be treated to a high level by the biological process. Often, these industrial wastes with high loads of BOD are treated in a manner equivalent to municipal wastes. However, in other cases, such as wastes from the metal finishing, chemical, petroleum, and steel industries, different treatment processes must be considered.

The processes and equipment for treatment of industrial and municipal wastes are very similiar in most instances. In some cases, the conventional type of treatment for municipal wastes can be modified to treat a specific type of industrial waste. Usually, an engineering fix is obtained from pilot studies which reveal those additional modifications or combinations of steps that are required to make the waste amenable to the equipment setup, or conversely, what currently available piece of equipment must be added to the existing equipment setup to treat the industrial waste.

But defining the level of secondary treatment of industrial wastes associated with its equivalent treatment of municipal wastes has not yet been accomplished with any reasonable validity, according to Burd. "Standards from many states contain the language that industrial wastes will be treated to the equivalent of municipal secondary waste treatment without ever defining what that is," says Burd.

Nonetheless, design engineers and others acquainted with the business may agree on a numerical value such as 80–90% removal of BOD for secondary treatment of municipal wastes. Furthermore, good design engineers can come up with plant designs today for any particular industry designed around the concept of industrial treatment equivalent to secondary treatment or the best practicable treatment, Burd reassures.

As yet, there is no broadly applicable definition of industry's equivalent treatment requirements being promulgated by the FWPCA. "We are currently investigating waste treatment definitions, says Burd. "FWPCA's first attempt to clarify attainable treatment levels was contained in the industrial waste profiles of last year's report, 'The Cost of Clean Water.' We realize additional information is necessary and have a program underway to accomplish this, but nothing has been published as yet," Burd explains.

Variances

A wide variance in individual water quality parameters such as dissolved oxygen and temperature is apparent from an inspection of state standards from different geographical areas of the U.S. In the Pacific Northwest, for example, higher numbers are placed on the dissolved oxygen requirement than in the eastern states. Differences in geography, climate, population, and industrial development account for some of the differences in this parameter, according to Burd. Furthermore, the significant variances in temperature usually range from a 2° F. rise, from background temperature in the summer, to as much as a 10° F. rise, from background temperature in the winter. As a general rule, FWPCA suggests that no more than a 5° F. rise from background be used in standards.

The recommendation of a passageway for fish and other aquatic life in standards is justified, according to Burd. Biologists report that if hot water extends across the width and depth of a stream, thereby creating a thermal barrier, fish will not penetrate this barrier and swim upstream. Therefore, a passageway must be established in the stream so that fish can swim around the hot spot in the water and then proceed upstream to spawn and to grow. This passageway would allow the fish to migrate, as well as the food that fish depend on for survival, from one part of the stream to another.

"The concept of a mixing zone is valid, not only for heated waste discharges, but also for sewage discharge or any industrial waste," says Burd. The language on mixing zones in today's standards applies outside of the mixing zone—the mixing zone being defined as a small area around the outfall line where conditions are not as desirable as downstream conditions where the treated waste is completely mixed with the dilution waters. For obvious reasons, a uniform definition for such a zone is impossible. The zone will depend on a number of regional variables including the flow in and the width of a particular body of water.

A discharge to the ocean could be expected to have less impact on its water quality than the discharge of an equal amount of waste to fresh waters because of the great amount of dilution that occurs. "In California, open ocean mixing zones are often defined as circular areas—300 feet in diameter—around the end of a discharge line," says Burd, based on his earlier professional experience as a member of California's Water Pollution Control Board. Again, he emphasizes that the mixing zone should not be used as a substitute for waste water treatment at the source, be it heated wastes or other water pollutants.

Advice

Recently, the National Technical Advisory Committee (NTAC) on water quality criteria, a special group of 86 consultants to the Secretary of the Interior, recommended criteria needed for specific water uses. NTAC's recommendations (ES&T, September 1968, page 662) will serve as a source book for water quality management on a national scale for a long time. Later, NTAC issued its second report which details those areas in need of additional research (ES&T, November 1968, page 998). Together, these reports will contribute to future refinements in standards.

The weaknesses in FWPCA's information are being filled as fast as the data can be generated. FWPCA conducts research at a number of its laboratories. For example, research on marine water quality requirements is the prime responsibility of FWPCA's National Marine Water Quality Laboratory at Narragansett, R.I. Similarly, research on fresh water quality requirements is the main activity of FWPCA's National Water Quality Laboratory at Duluth, Minn. (ES&T, August 1967, page 603). The Duluth laboratory spends a significant portion of its present budget investigating thermal effects on aquatic life. In time, relevant laboratory findings will lead to more refinements in standards.

In the future, FWPCA plans to make summaries of existing water conditions available to local officials, sportsmen, and other interested laymen for each of their particular interstate streams. The summaries will spell out the uses that can be made of waters, stream mile by stream mile, and the criteria necessary to protect those uses. Also, the summaries will provide general information on implementation and enforcement programs. Hopefully, by the summer of 1969, the first of these reports will become available, according to Burd.

Enforcement

"But standards alone will not improve water quality in the U.S., unless we execute effective plans of implementation, buttressed by vigorous federal-state enforcement programs when they are violated," Commissioner Moore told attendees of a seminar (Washington, D.C.) late last year. Under present laws, two courses of federal action are open for enforcement of water quality standards. The Federal Government can follow the already established procedure of conference, hearing, and court action, or it can move directly to bring court action against violators, according to Moore. But the direct court action must be predicated on a discharge which has violated the standards and must be preceded by a 180-day grace period to permit voluntary compliance on the part of the alleged polluter.

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Federal interest in estuarine zones builds

Interim measures must be developed until a long-range management scheme can be instituted

Estuaries constitute one of the most valuable of our natural resources—yet one that rapidly is being destroyed by landfill and pollution. The importance of estuaries is evident to the more than 50,000,000 people who live near them, use them for recreation, commercial fishing, trade, commerce and industry, mining, as a source of water, and for the disposal of wastes. Accompanying this widespread use is strong federal interest and activity.

The nation's first settlers set up housekeeping on our east coast estuaries: Hampton Roads, Va.; New York Harbor; and Boston Harbor. The estuaries not only gave the settlers a safe and natural port to use in commerce with the Old World but also a pathway into the New World. They were storehouses of finfish and shellfish and a good place to hunt water fowl. Villages and later cities used estuaries as seemingly inexhaustible sinks for sewage. If need be, an estuary could be changed to accommodate a port or a dump. Nobody particularly worried about conflicting uses nor the consequences of misuse—these considerations had to wait until the twentieth century.

Worth of estuarine zone

There are between 850–900 estuarine systems around the coastal periphery of our country. The coastal zone is a place where the land meets the sea, yet it is not the sea and not the land; it is part of a vital area that includes the mouths of rivers, vast reaches of the continental shelf, and, by Congressional definition, the Great Lakes.

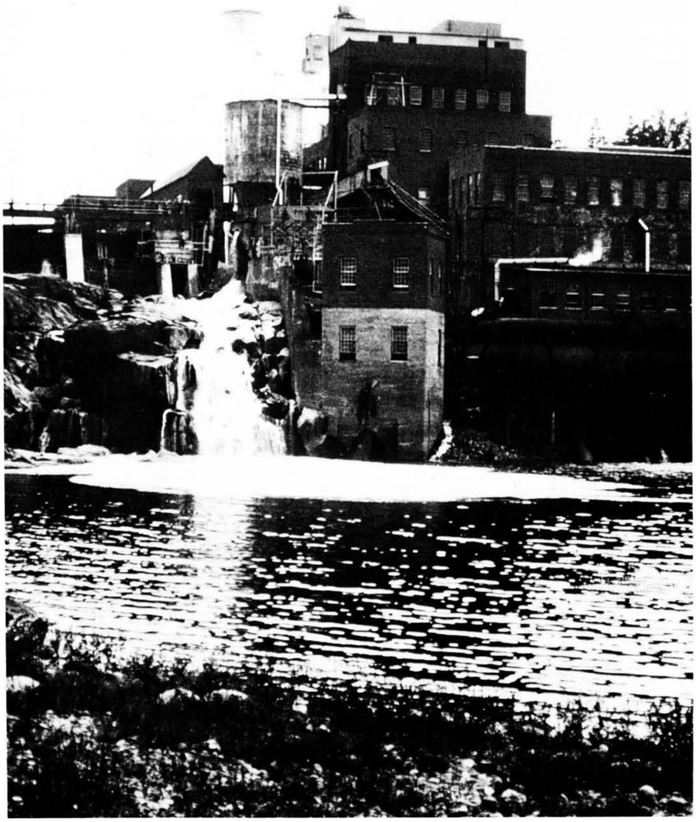
This article is based on a talk by Dr. Singer at the 60th Joint Annual Convention of the Oyster Institute of North America, Washington, D.C.

". . . a place where the land meets the sea, yet it is not the sea and not the land; it is part of a vital area. . . ."

Estuaries can be defined in many terms, depending upon the observer. There are physical, chemical, biological, and legal definitions, which may be enunciated in terms of tide, salinity, geography, or federal-state jurisdiction. What is a swamp to a housing developer is a bird breeding ground to the ecologist, or a recreation area to a duck hunter. In the Clean Water Restoration Act of 1966, Congress stated that, "The term 'estuarine zones' means an environmental system consisting of an estuary and those transitional areas which are consistently influenced or affected by water from an estuary such as, but not limited to, salt marshes, coastal and intertidal areas, bays, harbors, lagoons, in-shore waters and channels; and the term 'estuaries' means all or part of the mouth of a navigable or interstate river or stream or other body of water having an unimpaired natural connection with the open sea and within which the sea water is measurably diluted with fresh water derived from land drainage." By this definition, the estuarine zone includes the margins of the oceans.

Several years ago, the U.S. Department of Commerce—seeking to learn the value of the economic activity there for calendar year 1964—made an intensive study of the U.S. continental shelf. Eight major economic activities were identified: mining and petroleum; marine engineering; recreation; health and welfare; transportation; food and agriculture; defense and space; and research and development. The level of economic activity was estimated at $21.4 billion, a total that included operating expenses, investments, and income. A little more than half the money was spent for transportation activities; nearly $4 billion was spent for recreational activities; and about $330 million was the dockside value of the U.S. fishery catch from the con-

". . . our estuarine areas are limited . . . in their ability to absorb abuse."



tinental shelf area. The harvest of shellfish constituted the largest single portion of the U.S. fishery catch value, about 38%. If the investment for harvesting and processing the entire U.S. fishery catch for 1964 were included, then the total economic activity in fisheries rose to about $1.4 billion, a very respectable industry.

We cannot easily assay the nation's estuaries and estuarine zones. How can we assign dollar-values to the relaxation achieved by sportfishing in the tidal waters, swimming, surfing, skin diving, pleasure boating, or contemplating nature in solitude?

Demands on the estuarine zone

As the economic value of the estuarine zone rises, and population pressure increases, conflicting and competing uses of the estuaries become dominant. Today, we have almost six times as many people in the U.S. as we had a century ago. Since all of these people, in some fashion, call upon, and derive some benefit from, the estuarine zone, the nation has been forced to recognize that what it had in surplus, it now has in jeopardy. Even seemingly unrelated uses of an estuarine zone can have dire consequences; a solution to one irritating problem may engender far more pressing problems. For example, a pesticide that helps cherries grow in unblemished splendor in a Michigan valley orchard could result, under certain circumstances, in a mass of dead Coho salmon on the banks of Lake Michigan. While supertankers transport oil economically to all parts of the world, a bit of carelessness resulting in an oil spill can fill nearby beaches with the carcasses of thousands of oil-drenched waterfowl and suffocate much of the shellfish. Modifications of estuaries through dredging operations, filling in for real estate development, the outpouring of wastes from a city, fertilizer from nearby land—all are capable of disfiguring and destroying an estuarine zone.

Many people do not realize what happens to the ecology of an estuary when modifications are made in the waterway. Unfortunately, even when they do understand the consequences, the short-term, rather than the overall or long-term gain, may be the overriding reference for making such modifications.

More intensive uses of our estuarine zone are being planned continually:

- Bigger and more nuclear-fueled power plants, are being located on the coasts because they require very large quantities of cooling water.
- Increased desalting of estuarine and coastal waters, as technology improves, is creating brine, heat, and radioactive waste disposal problems; but desalting also gives water to cities and to arid lands.
- Increased pressure for housing and commercial sites in estuaries is stimulating the filling in of marshes and bays, and resulting in soil erosion and runoff of wastes from urban areas.
- Increased recreational demands, increased channel dredging for marinas and harbors, and shoreline modifications are promoting beach development.

Need for optimum use

Often, the opportunities for short-term gains can be very persuasive. A major company recently requested a lease from the Georgia Mineral Leasing Commission to conduct extensive phosphate mining operations along the Georgia coast. Reports indicate that the firm must remove between 70-120 feet of overburden to get at the phosphate deposit. The overburden would presumably be deposited in a coastal marsh area. The company involved says it will return the coastal region to its natural state, which, incidentally, would be very difficult to do. More to the point, though, is whether the immediate gain is worth the sacrifice; whether, in fact, the suggested enterprise is in the public interest. There are many problems in making such a judgment. We do not know the economic value of the Georgia coast as nursery grounds for fish and as recreational areas; it is possible that the mining of phosphates could trigger a series of red tide blooms, which could easily kill the state's fishing and tourist industry. Conceivably, the marshes and beaches could be returned to their original state if they were not obliterated or changed in character. I suggest that anybody who desires to change the environment should do so only with as much knowledge as possible of the implications of the change. These should be clearly drawn for the governmental bodies involved and for the people who will be affected.

What this example illustrates is that we must learn how to make optimum use of our estuarine areas. Obviously, they are limited in extent and in their ability to absorb abuse. They are also being called upon to serve more and more masters, under more and more difficult conditions. This brings forth the now accepted notion of multiple use of the coastal zone under which compromises are introduced in order to permit competing uses to coexist. Harbors and healthy oysters can coexist, for example, if pollution levels are held down; similarly, a properly designed sewage treatment plant and a swimming facility can coexist in the same area. Water quality is the common denominator for multiple use of the coastal zone. Here is an area where the Federal Government and the states can cooperate to produce a management system to advance the public purpose.

Marine commission and council

The Federal Government has been giving strong attention to the problems of estuarine zones. Two groups — the Commission on Marine Science, Engineering, and Resources; and the National Council on Marine Resources and Engineering Development—have made major efforts in surveying activities in these zones, and in formulating recommendations to use the zones in the best possible ways. To this end, the marine commission has completed a study that makes long-range recommendations to the President and the Congress. Meanwhile, the marine council, chaired by the Vice President, through its Committee on Multiple Use of the Coastal Zone, is coordinating the many coastal zone interests of many federal agencies and offices.

Army Corps of Engineers

The U.S. Army Corps of Engineers is one of the strong influences in the nation's estuaries. The Corps has sole authority to grant or deny permits for dredging and filling in navigable waters, based on the Rivers and Harbors Act of 1899. This Act is concerned only with navigational aspects, but more recent federal regulations have given the Corps the responsibility to prevent undue destruction of the nation's resource-rich estuaries as well, at least in the Corps' permit-granting activities. As a result, the Corps states: "The determination as to whether a permit will be issued will be based on an evaluation of all relevant factors, including the effect of the proposed work on navigation, fish and wildlife, conservation, pollution, and the general public interest. The Corps will accept comments on these factors, which will be made part of the record and will be considered in determining whether it will be in the best public interest to grant a permit." Yet whether the Corps can use other than navigational considerations in denying a permit has not been fully tested in court.

The Fish and Wildlife Coordination Act, amended in 1958, requires the Corps, and any other private or public agency needing federal permission to alter the course of any body of water, to consult both the Fish and Wildlife Service of the U.S. Department of the Interior and the Wildlife Resources Office of the affected state. The Act requires that the recommendations of both these resource agencies regarding the wildlife aspect of the project be explicitly considered in the planning.

In another action to help preserve our estuaries, Interior and the Army Corps of Engineers signed an agreement in 1967 to combat pollution in the dredging, filling, or excavation of navigable waters of the U.S. Field representatives of Interior and the Corps confer before the Corps decides whether to grant a permit affecting any navigable water.

Water quality and clean water acts

The next decade will be critical in the preservation of the estuaries. If we delay action until we fully understand how an estuary behaves and reacts to changes, we may be too late. The estuaries may become stagnant, putrid pools able to support only microscopic life and fit only to be filled for real-estate development. Fortunately, we have the legal authority available now for a vigorous program, as well as full Presidential and Congressional support to get on with the job of preserving our natural resources.

Congress created an effective instrument for action when it required that water quality standards be set for all interstate waters. Congress defined these waters in the Water Quality Act of 1965 to include all coastal waters. All of the states, the District of Columbia, Puerto Rico, Guam, the Virgin Islands, and the Delaware River Basin Commission have submitted water quality standards. Most have been approved as federal standards. The remainder are under active review by the Department of the Interior.

The standards identify uses of the waters, including agricultural, municipal, industrial, recreational, and fish and wildlife use including shellfish; they indicate the water quality standards needed to support each use; and they include plans to implement and enforce these standards. Vigorous, cooperative state-federal enforcement and implementation of these standards will upgrade water quality in the nation's estuaries.

Both the President and the Congress realized it was necessary to set an example for industry and the states in helping preserve the nation's natural environment. President Johnson, in mid-1966, issued Executive Order 11288, which seeks to keep federal agencies themselves from changing the quality of the nation's water and waterways. The order insists—it does not merely ask—that all federal polluters take corrective action. Further, the order requires that water quality be an important consideration in the planning, construction, and operation of all water resources projects, including new activities as well as additions and rehabilitation. The Executive Order commits the federal establishment to what the states are requiring of their cities—secondary treatment of wastes.

Controlling pollution and meeting water quality standards are costly. Consequently, the Clean Water Restoration Act of 1966 authorized \$3.5 billion to be spent over a four-year period to aid construction of municipal waste treatment plants. This money will help remove the backlog in construction of waste treatment plants, and control the municipal and industrial pollutants that might otherwise reach our estuaries.

In addition to enforcing water quality standards, the Secretary of the Interior may authorize a conference to enforce abatement of pollution when the pollution occurs in an interstate context, either on his own initiative or at the request of a governor of any state involved in an intrastate situation. Forty - five enforcement conferences have been initiated, 14 of which directly affect estuaries—Potomac River;

Raritan Bay; Puget Sound; Boston Harbor; Escambia River; Pearl River; Merrimac River; Mississippi River; Blackstone and Ten Mile Rivers; Savannah River; Hudson River; Moriches Bay and the eastern section of Great South Bay off Long Island; Penobscot River and Upper Penobscot Bay; and the eastern New Jersey shore from Shark River to Cape May.

National Estuarine Study

A comprehensive study of many aspects of estuaries, the National Estuarine Study was authorized by Congress in the Clean Water Restoration Act of 1966. Led by the Secretary of the Interior, with the cooperation of other federal agencies, the study will put forth an optimum management system for the coastal zones. Specifically, the completed report, due November 1969, will include: ". . . recommendations for a comprehensive national program for the preservation, study, use, and development of estuaries of the nation, and the respective responsibilities which should be assumed by federal, state, and local governments, and by public and private interests."

The recommendations will be based on extensive hearings, which are being conducted in the coastal states, to obtain the view of state and local government bodies, private organizations, and individuals. Note that Congress asks for recommendations for a *national* program, not a federal program.

There is little that the study cannot encompass: Congress was extremely broad in its prescription and called for a "comprehensive study of the effects of pollution, including sedimentation, on fish and wildlife, on sport and commercial fishing, on recreation, water supply and water power, and other beneficial purposes. Such study shall also consider the effect of demographic trends, exploitation of mineral resources and fossil fuels, land and industrial development, navigation, flood erosion and control, and other uses of estuaries and estuarine zones. . . ."

That is not all. The report will con-

". . . the nation has been forced to recognize that what it had in surplus, it now has in jeopardy."

tain an inventory of the nation's estuaries and an identification of areas where scientific knowledge is deficient. The three elements of the National Estuarine Study as it is envisioned today are:

- An inventory.
- An identification of scientific knowledge gaps.
- Recommendations for a national management system.

A comprehensive management system for the nation's estuarine zones, one that seeks to consider long-term as well as short-term benefits of resources, must arrange to:

- Understand estuaries.
- Direct an interim approach towards saving endangered ones.
- Work up a long-term management scheme for preserving them.
- Arrange for the most concerned governmental bodies to have the strongest voices in deciding the destiny of the estuaries.

Before we can manage, we must measure. Consequently, an important part of the National Estuarine Study will consist of a thorough description of estuarine areas and their resources, together with careful analyses of all present uses, and projections of future uses. This inventory will include assessments of the present and potential damage and losses to estuaries; in particular, the state of pollution and physical modification of the nation's estuaries will be identified.

The second element, that of identifying scientific knowledge gaps involved in estuarine processes, is essential for any management program. We particularly need to understand the ecological effects made by changes in the physical and chemical environment of estuaries. James Muir, the famed nineteenth century naturalist, said that whenever he picked up anything, he found it was attached to everything else in the universe. We will have to wait a long time before we see even a part of the web of these attachments. On the other hand, many actions will have to be taken based upon what knowledge we have available. It would be a poor doctor indeed who, because of his incomplete understanding of the whole of physiology, refused to administer first-aid to his patients.

Interim actions to protect estuaries

It will probably be many years before a national management system for estuaries is worked out, converted into legislation, and put into operation. Meanwhile, there will continue to be strong economic and political pressures on local communities and districts to accelerate the already increasing flood of development projects in estuaries. The pressure will be to make physical modifications to the estuaries, together with economic commitments, which are virtually irreversible. However, it is in the nation's interest—and probably in regional and local interests—to keep open as many of its choices as possible, at least until we know what we are foreclosing. To err on the side of conservation is advisable. The need, expressed in sharply-drawn terms, is to make sure there are estuaries left to manage when a national management system is adopted. To this end, all available existing legislation, executive orders, and regulations should be used by the Federal Government and by state and local governments to prevent — at least to minimize — further irreversible degradation of the estuarine zone.

State governments should strictly enforce their water quality standards, which have been set up for their estuarine and coastal zone waters; pollution abatement actions should be initiated whenever cause exists. States should be encouraged to adopt appropriate tideland legislation, following model legislation such as that in Massachusetts and New Hampshire. Construction projects in estuaries, which require permits from the Corps of Engineers, should be carefully and severely scrutinized by both state and federal agencies. It has been suggested that a permit be issued only when it conforms with a master plan. Lacking a master plan, states should be encouraged to develop a total or partial moratorium until one is developed. There is a precedent for this procedure in the State of California's Bay Conservation and Development Commission and in recent action by Florida's

"How can we assign dollar values to the relaxation achieved in the tidal zone?"

Internal Improvement Fund.

During recent Interior Department hearings, some witnesses suggested that all federal agencies involved in granting licenses—for example, the Atomic Energy Commission and the Federal Power Commission — or in granting planning or construction funds to municipalities or states — this includes agencies such as HUD, the Economic Development Administration in the Commerce Department, and the Department of Agriculture—should relate the award of grants to the prevention of estuarine degradation. The witnesses also suggested that disposal of federal surplus coastal lands to private developers should be suspended during this moratorium period.

Long-term estuary management

An interim plan is clearly necessary, but probably would not give adequate weight to the legitimate needs for development. We need to construct a long-range plan for managing our estuaries. Obviously, there are many legitimate uses for the estuarine zone. In general, no single interest should have the right to use these areas to the exclusion of others; rather, the management system that is set up should permit the most effective use.

A planning technique that might be used would be to devise an optimum resource utilization profile for each estuary based on a thorough analysis of the estuary's value. For example, certain estuaries, or portions of estuaries, might be set aside for aquiculture because of inherently favorable environmental circumstances. In other estuaries, land development might be permissible and consistent with recreation demands. Certain estuaries, on the other hand, might be singled out for preservation and acquired by the Federal Government or by state or local governments. (Such a course is being studied now by the Department of the Interior under Public Law 90-454.)

The difficult question is who does the planning and determines the system of designating uses? And at what level of government should this be carried out? Today, approximately 16 federal departments or independent agencies, 300 state agencies and 12 interstate agencies, plus several thousand local agencies have a significant involvement in estuarine uses or management. All of their efforts are highly focused. Nobody appears to be looking at the collective effect on the estuarine resources—as distinct from specific effects on a *water* resource or on a fish and wildlife resource, or on use as a waste disposal medium.

Since the pollution introduced at one point in an estuary has continuing effects elsewhere in the estuary, and since the dredging of part of an estuary can destroy the spawning grounds of fish that mature in waters miles away, we can see that spot zoning of these waters could not lead to an effective management system. If, as has been suggested, the level of government involved in managing estuaries for multiple uses should be commensurate with the range of interference in water uses, or, alternately, with the entire extent of the estuary, primary governmental responsibility for estuarine management would then go to the states; but the interests of local governments must be safeguarded, as well as those of the Federal Government, which represents the national interest. Interstate estuaries would be managed by the bordering states, through appropriate interstate agreements and compacts.

Federal Government's contribution

The Federal Government probably should not participate directly as a member of a management authority—possibly called the State Estuarine Management Authority — but should instead provide:

- National leadership.
- A clear definition of national goals and national interests.
- Guidelines to the states for assigning multiple uses, for management, and for enforcement. It is important, for example, that a State Estuarine Management Authority be independent of other state agencies, which represent special interests in the use of estuaries; that a mechanism be provided for adequate consideration of local interests most directly affected by zoning decisions; and that proper representation be given to the federal interests of navigation, national security, and international commitments.
- Funds on an equitable and matching basis to each state or interstate authority for its operation.
- Training opportunities, training grants, and other means for producing the management personnel for state authorities.
- A general format for a continuing inventory of the estuaries and coastal zones. The states probably should have the primary responsibility for the perpetual inventory of their estuaries and for studying their estuarine problems.
- A technique for value identification and appraisal in order to provide some objective standards for the rational zoning of estuaries.
- Studies that have general rather than local application. One example is a national port study that would be conducted by appropriate federal agencies. Ports and harbors are generally built and maintained to satisfy local and even regional needs. In the process of dredging, leveeing and diking, many vital estuarine resources have been destroyed. An appropriate study would define the nation's needs in terms of major ports, off-shore terminals, and other facilities for maritime commerce in the light of new maritime requirements. Perhaps the number of ports and harbors could be cut down radically and, consequently, some valuable estuarine areas saved or, at least, rejuvenated.
- A general environmental monitoring and prediction system. This would provide important data and services to the states and other governmental units for estuarine management work.

The states probably should have a major responsibility for studying the scientific problems peculiar to their own estuaries. The Federal Government should be concerned with whether these efforts are properly financed. Existing programs could be utilized, such as those of the National Science Foundation, the Office of Water Resources Research, the Federal Water Pollution Control Administration, and the Bureau of Commercial Fisheries. The Sea Grant Program, established a few years ago by Congress, may be suited for the support of local universities which may wish to engage in estuarine and near-shore marine research and engineering.

We have gone full circle. We started out with the familiar concept that often we do not appreciate what we have until we lose it. Our estuaries fall into this category; they are immensely valuable and they are endangered by pollution and irreversible physical modification. All levels of government—indeed, all individuals—have a great stake in using these areas in an optimum manner. To do this, there must be various interim measures so that we have viable estuaries left to manage by the time a long-range management scheme is instituted. Such a long-range management scheme would have to be based upon some effective use allocation, with full knowledge of an estuary's potential for development and its vulnerability to destruction. To obtain this information, we need to understand estuaries scientifically and technically, as well as in economic and social terms. We would use this information to construct an optimum management structure for the nation's estuarine zone to serve public and private needs in the best way possible. The National Estuarine Study will contribute to this purpose by providing recommendations for legislative action.

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Nuclear methods in air and water pollution analysis

Nuclear methods are well suited to the field of pollution analysis for a number of reasons. The sensitivities obtainable range from parts per million down to 10^4 molecules, and embrance the requirements of most pollution analyses. The chemical nature of the radioactive material can be controlled, and the method can become uniquely specific for the substance being determined. In fact, few other techniques offer the specificity of nuclear techniques. Furthermore, nuclear methods stand apart in their relative freedom from interferences. Radioactive materials are present in the environment, but such natural occurring radioactivity offers little interference to analytical techniques.

With the exception of oxygen, nitrogen, and magnesium, most elements have useable radioactive forms, providing unusual versatility. Like most instrumental methods, nuclear methods are fast, their speed depending only on accuracy desired and quantity of tracer available for measurement.

Simplicity of use and predictability are other advantages of nuclear methods. Each nuclear decay scheme is unique, a fact that often simplifies measurement. Properties of radioactive materials are well-known and follow definite mathematical relationships. Since these properties are a function of the nucleus, they are unaffected by the chemistry of the system. The ability to make relative measurements often simplifies the analysts' work, in contrast to the tedium involved in most analytical procedures utilizing physical measurements.

Nuclear methods also have the advantage of low cost. Many procedures involve only a few cents worth of radioactive material and equipment that costs less than $100. Even the highly sophisticated methods and equipment are no more expensive than those for other analytical techniques such as mass spectrometry, emission spectrometry, and infrared spectrometry.

Disadvantages of nuclear methods

Nuclear methods are not the complete answer to the pollution analysts' problems, because chemists, engineers, and technicians are seldom trained in theory and application of nuclear methods. Few pollution analysts have had even a two hour lecture course dealing with nuclear technology, let alone a course including some laboratory experience. Indeed, few schools offer such courses. Academic and industrial research labs are just now beginning to train personnel, mainly through short courses offered at the Oak Ridge Associated Universities and major state universities.

The second major hindrance to the adoption of nuclear methods involves adverse public reaction, often including the reactions of upper management, some research workers, and government officials. This opposition can prevent application of nuclear methods even though no health hazard is involved. The continuing public relations programs of AEC and an increasing number of enlightened technical and nontechnical people are diminishing this problem.

However, a good public relations or educational program still must be included in many large projects to prevent serious interference. One good approach is to strongly publicize the fact that federal regulations on use of fission-produced radioisotopes are being adhered to, or even bettered. This often alleviates many of the public's fears. But the paper work and red tape involved in compliance may exceed the technical problems, and so slow down the work at hand as to completely kill it. Experience with regulatory matters helps overcome these problems.

The last major problem of nuclear methods—one which is slowly disappearing—is availability of the proper tracer. More commercial concerns are producing tracers, and even foreign-made products are becoming available. As specific needs become known, complex radioactive compounds reach the market. Radioactive forms of most insecticides, for examples, now are available as stock items; two years ago they had to be specially synthesized.

Self-degradation of the tracer, impurities in the tracer, exchange, and the isotope effect are some of the minor disadvantages attached to nuclear methods. The increase in the number of technical articles dealing with nuclear methods proves that trained personnel using reasonable care can cope with these problems. In 1946, 1.1% of the articles in *Analytical Chemistry* were on nuclear methods; in 1965, the figure had risen to 7.4%. Similar increases are apparent in other technical journals. In the life sciences, radioisotopes are accepted just as any other tool or technique. Only the training and imagination of the user seem to limit applications.

Early history

The beginning of nuclear science can be traced back at least to Roentgen's discovery of x-rays in 1895. Subsequently, the nature and properties of radioactive materials unfolded rapidly through the work of Bequerel, Thompson, Wein, the Curies, and Rutherford. With Villard's discovery of gamma radiation in 1900, all simple modes of nuclear decay and their half-lifes became known. By 1915, the existence of isotopes, the nature of the alpha particle and beta decay, and mass energy equivalency (Einstein) were revealed.

In 1919, Rutherford observed the nuclear reaction:

$$^{14}N + {}^{4}He = {}^{1}H + {}^{17}O$$

This established transmutation and isotopes, and led to postulation of the existence of neutrons. Two of Rutherford's students, Cockcroft and Walton, developed an accelerator and, in 1932, accomplished the first artificial nuclear transformation:

$$^{1}H + {}^{7}Li = 2{}^{4}He$$

The first artificial radioactivity was produced a year later by the Joliets:

$$^{27}Al + {}^{4}He = n + {}^{30}P$$

From 1934 to 1938, Fermi studied the (n,γ) reactions of 68 elements and found 47 radioactive products. During the same period, Hahn and Meitner bombarded uranium with neutrons, hoping to produce element number 93. In due course, the uranium atom was split and the atomic era unfolded.

Not long after radiation and radioisotopes were discovered, scientists began to put them to practical use. X-rays became an important tool in medicine. Use of radioisotopes, which were less available, grew a little more slowly. The power of the radioisotope as a tracer lies in the fact that it satisfies the otherwise impossible criteria for sophisticated tracing:

- The tracer must be identical to the material being traced.
- At the same time, the tracer must be detectable—different in some measurable way from the material being traced.

The first application of radioisotopes as tracers came in 1913 when Hevesy and Paneth used radium D (an isotope of lead) to determine the solubilities of lead sulfide and lead chromate in water. Hevesy's work included the first tracer experiment in biology—he followed the movement of lead in a bean plant (1923); in 1924, he traced the movement of bismuth in a rabbit (1924)—the first tracer experiment using an animal. Hevesy used isotope dilution as an analytical method to determine lead content in rocks in 1931, and he and Levi used activation analysis to determine impurities in rare compounds in 1936.

The principle behind the use of radioisotope tracers is that radioactivity is a nuclear property—only the nuclei of the isotopes of an element differ. Since chemical properties are functions of electron clouds around the nucleus, radioactive isotopes generally can be expected to behave in chemical reactions like their stable counterparts.

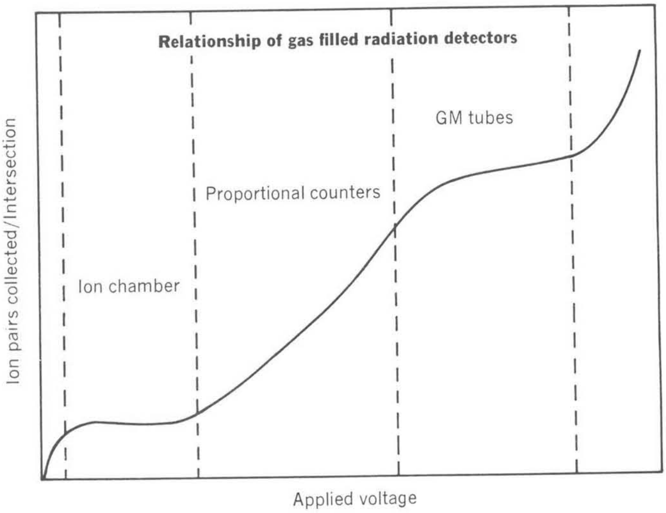


Figure 1

Because the radioactive and stable isotopes of most elements exhibit identical chemical behavior, the radioactive isotope makes a good tracer. However, hydrogen isotopes can show a large deviation from this principle because the radioactive isotope has three times the mass of the stable isotope. This large mass difference may produce different rates of reaction of ^{3}H compared with ^{1}H. With hydrogen, this isotope effect may be quite large, but except in rare instances, the mass of the nuclei involved is large enough to make the isotope effect negligible. In some cases, the isotope effect is helpful in explaining chemical reaction mechanisms. Relative measurement techniques can be used to compensate for the isotope effect in work using light element radioactive tracers.

Radioactive nuclei decay, or emit radiation, at a predictable rate which is expressed in terms of half-life. Each nucleus has its own particular kind of radiation:

- **Alpha particles**—nuclei of helium atoms.
- **Beta particles**—positive or negative electrons.
- **Photon**—x-rays or gamma rays.

The radiation from a given nucleus will have a specific energy or energy range. Thus, half-life, type of radiation, and energy of radiation uniquely identify an isotope and assure correct measurement.

Detection devices

Radiation can be detected by either of two major types of sensors:

- Ionization or gas-filled detectors
- Scintillators

In special cases, the detectors can also be photographic emulsions, solid state devices, or spark chambers.

Ionization detectors that are available include ion chambers, GM (Geiger-Muller) tubes, and proportional counters. In these detectors, radiation penetrating the gas-filled detector chamber produces ions which are collected by placing a voltage across two electrodes in the chamber. In the ion chamber, only ions formed by radiation are collected; thus, the electrical current is a function of the amount of radiation.

The higher voltages used in proportional and GM detectors produce secondary ionization by accelerating the primary ions, which then collide with other gas molecules. This ion multiplication results in each radiation interaction in the chamber producing a voltage pulse from the detector. Proportional detectors give millivolt pulses, while GM tubes give pulses as large

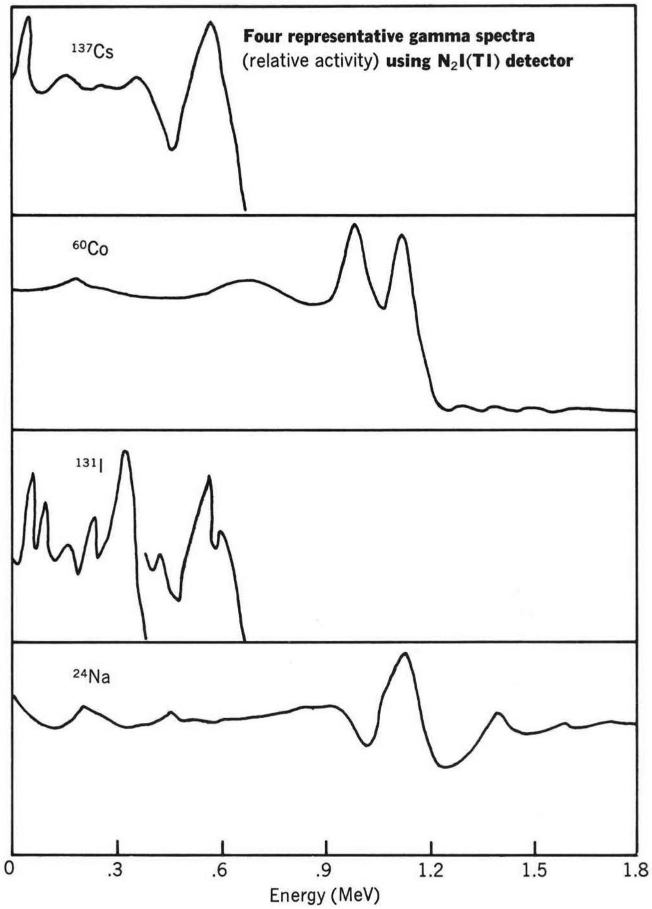

Four representative gamma spectra (relative activity) **using $N_2I(Tl)$ detector**

Figure 2

as 10 volts. GM tubes are very sensitive because any radiation interaction produces an output pulse. However, GM tubes do not discriminate as to the kind of radiation or its energy. Proportional counters and ion chambers do discriminate.

Scintillation counters also discriminate as to energy of radiation. In these detectors, materials such as NaI(Tl), ZnS, anthracene, and diphenyloxazole convert radiation energy into light. Photomultiplier tubes observe the light and convert it into electrical pulses; the amplitude of the pulses is proportional to the amount of energy deposited in the scintillator by the radiation interaction. NaI(Tl) crystals are used to produce gamma spectra, and solutions of organic scintillators are used to count beta particles. Both techniques result in excellent sensitivity.

Nuclear techniques

The extreme sensitivity with which radioactive materials may be detected and measured accounts for only part of the value of nuclear analytic techniques. The existence of a useable radioactive form of most elements, coupled with the nearly identical behavior of most radioactive and stable forms, gives the analyst one of the most powerful tools of his trade. With it he can trace an atom in a compound; a functional group; a compound; a class of compounds; or a phase, simply by choosing the proper radioactive material and detector system. As we have seen, important assumptions are implicit in the application of radioactive tracers:

- Radioactive and stable species behave identically.
- Radiation produces no change in the system.
- In biological systems, the radiotracer or carrier produces no physiological changes.
- The tracer has no labeled impurities.
- Only labeled atoms are traced.
- Tracers produce data unavailable or inconvenient to obtain by other methods.

Isotope dilution

A number of nuclear techniques are available to the pollution analyst. One of these, isotope dilution, offers an alternative to quantitative recovery of very tiny amounts of material from a sample or one component from a complex and closely related mixture of similar compounds. A small quantity of the radioactive form of the material to be determined is added to the sample mixture. Once the pure material is isolated and measured, the recovery yield can be calculated from measurement of the radioactivity. In this way, the yield can be corrected for losses in the separations needed to obtain the pure material. Isotope dilution, in fact, allows the analyst to make quantitative analyses without quantitative recovery.

This formula describes the correction made using the tracer:

$$\text{wt.}_{\text{unknown}} = \text{wt.}_{\text{tracer added}} \times \left(\frac{\text{Sp. Act.}_{\text{tracer}}}{\text{Sp. Act.}_{\text{recovered compound}}} - 1 \right)$$

or

$$= \text{wt.}_{\text{recovered compound}} \times \left(\frac{\text{Act.}_{\text{added}}}{\text{Act.}_{\text{recovered compound}}} \right) - \text{wt.}_{\text{tracer added}}$$

Because measurement of radioactive material is extremely sensitive, the tracer can be added in small amounts compared to the quantity of material being traced. The formula then simplifies to:

$$\text{wt.}_{\text{unknown}} = \text{wt.}_{\text{tracer added}} \times \left(\frac{\text{Sp. Act.}_{\text{tracer}}}{\text{Sp. Act.}_{\text{recovered compound}}} \right)$$

or

$$= \text{wt.}_{\text{recovered compound}} \left(\frac{\text{Act.}_{\text{added}}}{\text{Act.}_{\text{recovered}}} \right)$$

Determination of the gamma-isomer

of benzenehexachloride in insecticides is a straightforward illustration of the technique. As little as 0.6 μc of the gamma-isomer, tagged with ^{14}C or ^{36}Cl, is added to a mixture of the technical or commercial material. The pure gamma-isomer is obtained by solvent extraction or column chromatography; constant specific activity indicates recovery of a pure specimen. The activity of a known amount of the recovered isomer is measured in the same fashion as the activity of the added tracer is measured; a simple calculation gives the amount of the gamma-isomer present.

The determination of fluorine contamination of tooth enamel illustrates the sensitivity of this method. As little as 0.1 p.p.m. F^- is measured in a few minutes by adding carrier-free ^{18}F as F^- to a solution of the enamel. The tagged solution leaves F^- on a glass slide after pH adjustment. The amount of $^{18}F^-$ left is inversely proportional to the F^- content of the sample. The quantity is determined by comparison with a set of standards.

This variation on the normal isotope dilution technique is not the only possibility—reverse, double, saturation, and substoichiometric isotope dilution methods also have been used. The National Bureau of Standards excels in these techniques, reporting sensitivities for metal ions in the 10^{-4} g./ml. to 10^{-10} g./ml. range with good accuracy. In one example of this work, as little as 30 μg of Cl^- is measured by adding $^{36}Cl^-$ and precipitating with less than a stoichiometric amount of Hg^+. Even lower measurements should be possible with greater specific activity of $^{36}Cl^-$.

Radiorelease

Radiometric analysis occupies a niche closer to the traditional techniques of the pollution analyst. One radiometric technique, radiorelease, has already been applied to air and water pollution problems. Radiorelease has the advantage of being able to produce continuous measurements in an automated system, also as well as providing a sensitive laboratory technique.

In radiorelease analysis, the material being determined replaces or releases a radioactive substance from a matrix. The radioactive substance is collected and counted, and the measured activity relates directly to the quantity of material producing release of the radioisotope. This technique can be quite selective, or even specific, as well as extremely sensitive.

One of the more promising approaches to radiometric analysis involves kryptonates. The isotope ^{85}Kr is encaged in a crystal lattice of hydroquinone by crystallizing from solution under a pressure of 60 atm. Any strong oxidant destroys the clathrate, or cage, of hydroquinone-krypton, and releases ^{85}Kr. Separation or removal of unwanted oxidants by gas chromatography or appropriate absorbants permits the desired oxidizing agent to be detected at the p.p.b. level in air. This technique has been used for O_3, SO_2, NO_2, Cl_2, and ClO_2, both in batch and continuous analysis. Release of absorbed ^{85}Kr from various materials gives a measure of H_2 at the 0.01% level, or F^- at 2μg/ml.

Similar techniques provide for measurement of SO_2 by release of ^{131}I; dissolved oxygen in water by releasing ^{204}Tl; $Cr_2O_7^{-2}$ water tracer by releasing ^{110}Ag; and coliform bacteria by producing [^{14}C] CO_2 from [^{14}C] formates. Sensitivities at the p.p.m. level or below have been reported for these methods. By using higher specific activities, sensitivities as low as one part in 10^{12} are possible. For example, few cells of coliform can be detected in about four hours, including incubation time.

Radioisotope derivative analysis

Radioisotope derivative analysis has good specificity, sensitivity well below the p.p.m. range, and is quite direct and predictable. In spite of this, and in contrast with radiorelease, few uses of the method related to pollution analysis have been reported.

Radioisotope derivative analysis works this way: A stable compound is formed in a reaction between the substance to be determined and a tagged reagent. After reaction is complete, excess reagent is removed, and measurement of residual activity gives the quantity of substance present in the sample through the relationship:

$$\text{mmol unknown} = \frac{\text{Sp. Act.}_{\text{derivative}}}{\text{Sp. Act.}_{\text{reagent}}}$$

This technique is applicable to less than microgram amounts of ions or compounds separated by such techniques as paper and thin-layer chromatography. Metal ions can be precipitated on their chromatograms with reagents such as [^{35}S] sulfide or -sulfate, [^{32}P] phosphate, or [^{131}I] iodide or -iodate. Sensitivities as low as 0.01 μg for metal ions separated by paper chromatography are possible using radioactive precipitants.

The excellent sensitivity possible with radioisotope derivative analysis is shown best by work outside of pollution analysis; end-ground analysis in nylon using 20–50 mg. samples is a good example. Similar problems of sensitivity and sample size exist in pollution and could be solved by derivative analysis.

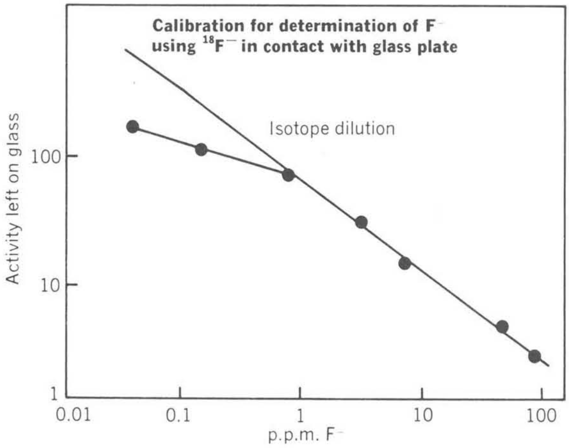
Radiometric titration

Radiometric titration offers the advantages of sensitivity, speed, and automation to the pollution analyst. However, this technique has not yet been incorporated into general procedures in pollution analysis. Using a radioactive reagent, titrations of Cl^- and SO_4^{-2} can be performed at the 10–50 p.p.m. level under conditions that preclude the use of the usual indicators. The radioactive reagent acts as its own indicator, or can be used as the indicator when stable reagents are used. End points can be located by making two additions of reagents before and two additions after the end point. By taking a count on the supernatant liquid after each addition, the end point is located as it is in conductimetric titration. Application to precipitation reactions such as Cl^-, I^-, CrO_4^{-2}, and CN^- by Ag^+; Cl^- by Hg_2^{+2}; Ba^{-2} and Pb^{+2} by SO_4^{-2}; and F^- by Ca^{+2} have been reported with sensitivities in the 1–5 p.p.m. range.

Method studies

Of considerable importance to the pollution analyst is the use of radioisotope tracers to calibrate analytical methods, to study reaction stoichiometry, to determine sample losses, separation efficiencies, contamination, and interferences, and to prepare analytical standards.

Many standard analytical methods have been examined using radiotracers. This examination becomes more necessary when a given method is pushed to lower sensitivities or is used to handle varieties of matrices and small sample sizes. A good example is the



Fremlin, J. H., Hardwick, J. L. *et. al.*, *Nature, (London)* **180**, 1178 (1957)

Figure 3

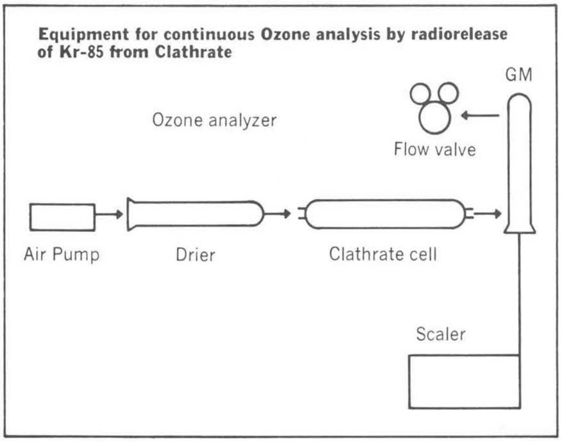


Figure 4

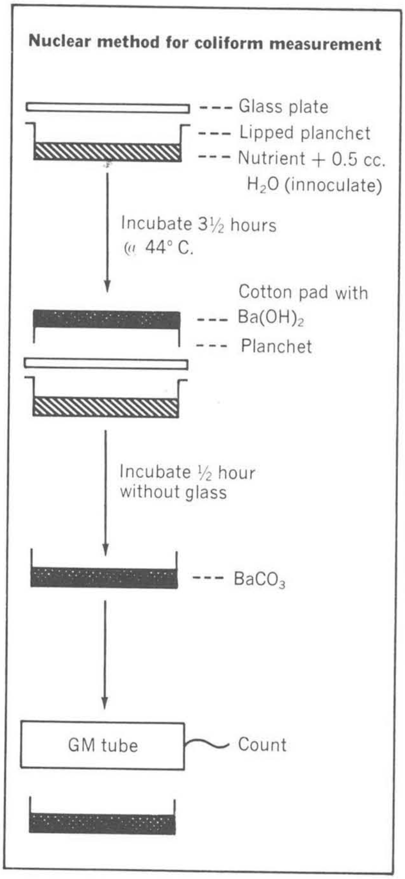


Figure 6

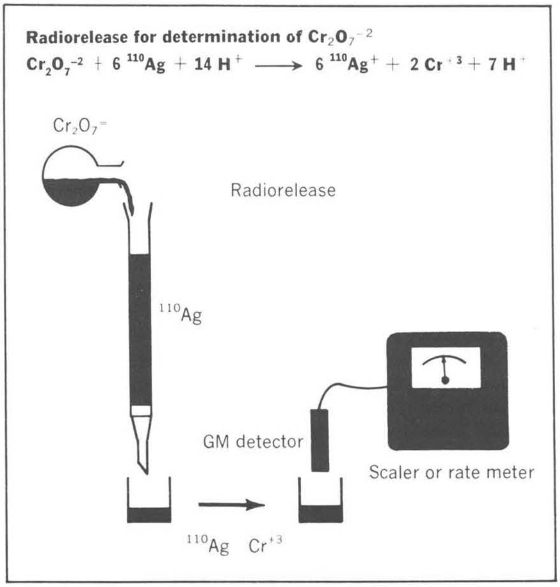


Figure 5

analysis for amine groups using dinitro-fluorobenzene. While not directly applicable to pollution work, it does illustrate the use of tracers to study reaction stoichiometry and also to calibrate an analytical procedure.

Another common method study uses a radiotracer to establish and follow losses of a material being analyzed. By adding a minute amount of tracer, the analyst can readily locate sample losses at any point in a procedure and correct his final measurement for the losses. For example, vaporization of metals from samples being analyzed by arc spectroscopy can be measured by the use of radiotracers; tracer methods have also proven that different ashing procedures for the concentration of Sb, Cr, Fe, Pb, and Zn samples show quite different losses. Of particular importance to water pollution analysis are recent studies indicating that traces of metal ions are adsorbed from solution on the walls of storage containers. Losses to glass and plastic container walls, including Teflon, can be almost 100% over long storage periods. With the insight possible with tracers, procedures can be established to minimize such losses when they are known to exist.

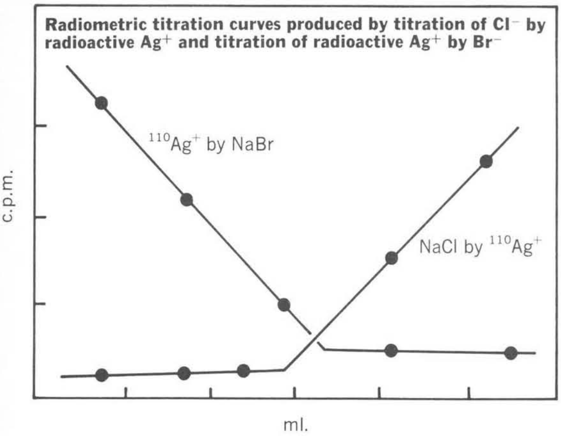
The major use of radiotracer analysis is to determine the efficiency, as well as the losses, of various separation processes. Almost any conceivable separation technique can be studied by radiotracer methods, including all the separation and concentration techniques of air and water pollution analysis. Precipitation and coprecipitation, filtration, electrodeposition, crystallization, zone refining, sublimation, distillation, adsorption, extraction, and chromatography are some of those that have been documented. Many of these studies have evaluated the technique at trace levels. Radiotracers provide the sensitivity necessary to accurately measure less than 1% losses or incomplete separations at trace concentration levels.

Tracer studies cover work as classical as the precipitation of $BaCO_3$, iridium from solution with platinum group metals, and magnesium as $MgNH_4PO_4$, and as modern as the use of organic precipitants. Changes in the nature of the precipitation easily become apparent when tracers are used, and the sensitivity of tracer measurements presents the analyst with the necessary tool for coprecipitation studies. Adding a minute amount of tracer to the real sample, and measur-

General license quantities of radioactive isotopes

The radioisotopes listed below are available to knowledgeable individuals without a specific USAEC license. An individual may possess and use as many as 10 of the quantities below if they are not combined, human consumption is prevented, and proper precautions are used in handling. These are sufficient quantities for many analytical purposes.

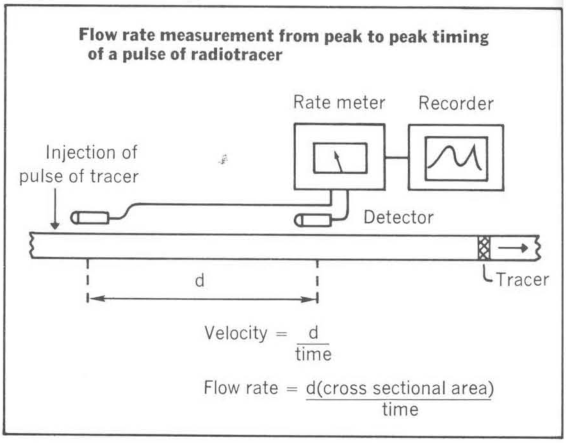
	microcuries/package	
Radioisotope	**any form**	**sealed source**
Sb-124	1	10
BaLa-140	1	10
Ca-45	10	10
CeBa-137	1	10
Cr-51	50	50
Cu-64	50	50
Ga-72	10	10
Au-198	10	10
I-131	10	10
Fe-55	50	50
La-140	10	10
Mo-99	10	10
Nb-95	10	10
PdRh-103	50	50
Po-210	0.1	1
Re-186	10	10
Rb-86	10	10
Ag-111	10	10
Na-24	10	10
SrY-90	0.1	1
Ta-182	10	10
Tl-204	50	50
W-185	10	10
Y-90	1	10
As-76	10	10
CdAg-109	10	10
C-14	50	50
Cl-36	1	10
Co-60	1	10
F-18	50	50
Ge-71	50	50
H-3	250	250
Ir-192	10	10
Fe-59	1	10
Mn-52	1	10
Ni-63	1	10
Pd-109	10	10
P-32	10	10
K-42	10	10
Rh-105	10	10
Sc-46	1	10
Na-22	10	10
Sr-89	1	10
S-35	50	50
Te-127	10	10
Sn-113	10	10
V-48	1	10
Zn-65	10	10



Radiometric titration curves produced by titration of Cl^- by radioactive Ag^+ and titration of radioactive Ag^+ by Br^-

Langer, A., *Anal. Chem.* **22**, 1288 (1950)

Figure 7



Flow rate measurement from peak to peak timing of a pulse of radiotracer

Figure 8

ing radioactivity in the filtrate, makes a very sensitive and accurate check for completeness of precipitation under true analysis conditions.

Efficiency of smoke filters can be determined by radioactive tracers. Tracers can point out electrodeposition of contaminant metals as well as incomplete plating. In zone refining, the use of radioactive tracers and reaction activation of the impurities shows the amount and location of trace impurities through autoradiography.

Sublimation and distillation problems also succumb to the application of tracers. The material being recovered, or the entrainment of residue, is followed easily. For instance, in the removal of fluoride from phosphate, the conditions giving complete recovery of fluoride can be determined using tagged fluoride, and entrainment of as litle as 0.0045% of the phosphate can be followed using labeled phosphate.

Solvent extraction is another fertile field for tracer separation studies. Separation and concentration of many metal ions have been studied. Sensitivities as low as 10^{-9} moles are possible with tracers. Partition coefficients can be determined by counting samples of the two phases involved. The completeness of separation and reproducibility of the technique involved is easily measured, even at concentrations below present spectral quantitation techniques.

Radioactive tracers are finding considerable use in chromatography. They can identify substances separated by paper or thin-layer chromatography when parallel runs of unknown and knowns do not work. Autoradiography pinpoints the tracer without disturbing the chromatogram. Losses by irreversible adsorption can be studied and tailing can be detected without interference from a blank. The tracers also offer the advantage of external continuous monitoring of the effluent from column chromatography. Tracers can give calibrations in gas chromatography without disturbing the qualitative or quantitative analysis being carried out. Loss and degradation on gas chromatography columns is easily noted using tracers.

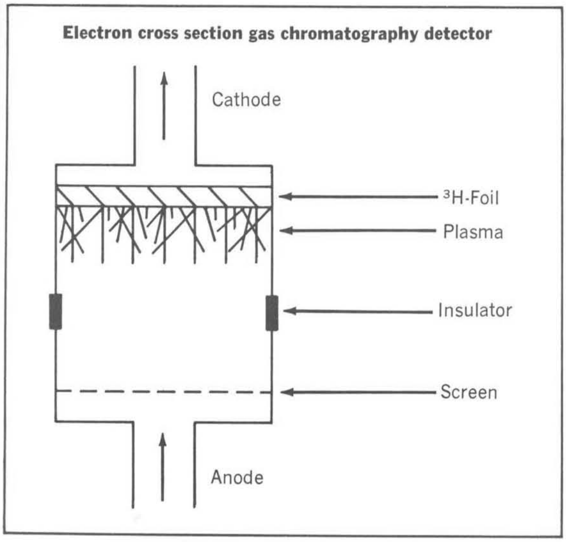
Radioactive tracers are playing an important part in preparation and purification of chemical reagents. Without them, ultrahigh purity reagents for trace analysis probably would still be unknown. Preparation of analytical standards for new materials is a problem that has come to the polymer chemist but not yet to the pollution analyst. Radioactive materials have aided in preparation of unambiguous standards for new materials when no other satisfactory standards were available.

Tracing

Tracing stands as one of the most unique applications of radioactive materials, and tracing of almost every conceivable substance or system is reported in the literature. Much of this work either relates to problems similar to those met in air and water pollution control, or specifically deals with solution of a pollution problem. In general, these problems require measurements of flow rate, description of flow patterns, calculation of system volume, location of contaminant origin, and determination of rate of contaminants added to a system. Examples of flow rate measurements of interest in pollution control include studies of sewage plant output, industrial plant discharges of liquid or gaseous wastes, and auto exhaust. Such flow rates can be measured by two methods:

- **Peak to peak timing** utilizes a pair of radiation detectors a known distance apart along the flow system. A pulse of radioactive tracer is added upstream of the two detectors. The time for passage of the tracer between detectors permits calculation of flow velocity; knowledge of the crosssectional area of the system yields volumetric flow rate:

$$\text{Volumetric flow rate} = \left(\frac{\text{distance between detectors}}{\text{time between radiation peaks}}\right) \times (\text{cross-sectional area})$$



Electron cross section gas chromatography detector

Figure 9

- **The total count method** is applicable to systems in which cross-sectional areas are unknown or irregular. In this technique, a known amount of tracer introduced upstream from a single calibrated detector produces a radiation reading inversely proportional to the system flow rate. The faster the system flows, the less radiation is detected. The tracer must be introduced far enough upstream to permit complete mixing in the system:

$$\text{Volumetric flow rate} = \text{detector calibration factor} \left(\frac{\text{activity introduced}}{\text{counts detected}} \right)$$

$$\text{detector calibration} = \frac{\text{counts/unit time}}{\text{activity/volume}}$$

In much the same fashion, flow patterns of contaminants from sewage and industrial plants in rivers, bays, and settling tanks are traced. Effluents can be followed with radiation detectors far past the limits of dilution for nonradioactive chemical or biological components. Reliable data are obtained miles from the contaminant source; even vertical profiles can be established.

One could list other examples:

- Leaks from sewers and water lines can be located precisely.
- Particulate material in streams or the atmosphere can be tagged and followed for considerable distances.
- Toxic materials in soil, food, air, or water can be followed into biological systems and their residence time and chemical fate determined.
- In a few cases, naturally occurring radioactive tracers point out the answer to a pollution problem. Both carbon-14 and hydrogen-3 occur in nature. Their concentrations in air and water depend upon the history of the system. A knowledge of the concentration of the natural tracers shows the source of encroachment into coastal aquifers and stratification of water in lakes.

Radiation absorption

Nuclear radiation absorption finds only a few applications in air and water pollution studies. The important applications are in moisture measurement and gas chromatographic detectors. Gages using x-ray emissions from ^{109}Cd can measure continuously the silt content of streams and rivers. Measurement of the density of the atmosphere is also possible.

Moisture content measurement of a variety of materials uses the property of hydrogen either to stop electrons or to thermalize neutrons. Hydrogen gages using beta sources (electrons) are applicable only to low atomic number materials—usually giving hydrogen-carbon ratios. Thermalization of neutrons is applied more widely, being used for moisture content in minerals and fertilizer, as well as for hydrogen content.

The use of beta radiation sources in gas chromatographic detectors is well known. The ionization and electron-capture detectors, with their extreme sensitivity, are used for many air pollutants, and insecticide studies utilize the beta particle from isotopes such as tritium ^{3}H, ^{63}Ni, and ^{90}Sr as excitation sources. Such detectors carry the major load in the analysis of volatile pollutants.

Activation analysis

In the area of elemental analysis, no other instrumental technique offers the sensitivity and versatility of activation analysis. For trace analysis, no other technique possesses the freedom from reagent contamination by the element being analyzed. Activation analysis also possesses advantages of speed, simplicity, specificity, and nondestruction of the sample.

This method involves making radioactive those elements of interest in the sample. Generally, exposure to neutrons in a nuclear reactor produces the radioactive species. The reagent is the neutron, and the only sample handling necessary is encapsulation in polyethylene. Thus, addition of foreign elements or increasing the amount of determined element in the sample is avoided.

After activation of the sample along with a standard, the induced activities are measured. The quantity, energies, and half-life of the induced radiations are determined using gamma spectrometry. The energy and half-life of the radiations from the sample identify the element activated; the quantity of the radiations relate directly to the quantity of the element. Calculations use the simple relationship:

$$\text{wt.}_{\text{element}} = \text{wt.}_{\text{element in standard}} \times \left(\frac{\text{Activity}_{\text{unknown}}}{\text{Activity}_{\text{standard}}} \right)$$

Using high flux reactors, sensitivities for many elements are well below 1 p.p.m. in 1 gram samples. Other irradiation techniques such as high energy photons and charged particles can be used but, as yet, are not as useful generally as the neutron bombardment.

To get maximum sensitivity, some elements require chemical separation after irradiation. Separation after irra-

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diation avoids contamination of the sample. In fact, a known quantity of the element being detemined is added to the sample to act as a carrier for the small amount of radioactive material. The element then is recovered in an appropriate pure form and its radioactivity measured. Chemical yield of the carrier corrects the radioactivity measurement for losses in the chemical separation. Such procedures produce sensitivities in the nano- and picogram range.

Application of activation analysis to the field of air and water pollution is still in its infancy. Air has been analyzed for argon, beryllium, iodine, bromine, chlorine, and selenium. Argon, arsenic, barium, bromine, chlorine, calcium, iodine, potassium, manganese, selenium, sodium, strontium, sulfur, thorium, and zinc and be determined in water. In addition, considerable work has been done with trace elements in biological materials and should be applicable to pollution in the environment. Activation analysis also permits use of nonradioactive tracers to follow air and water movements without the tracer contributing to a pollution problem.

Future prospects

The brightest prospects for nuclear methods probably are in the areas of method studies and automation of analyses. Radioactive tracers offer sensitivity, uniqueness, and simplicity in examining an analytical method. Generally, limited quantities of radioisotopes are available without a specific AEC license. These quantities are large enough to permit study of many analytical methods.

Tracers will be used almost routinely in the future to check a new analytical method or to extend an existing method to new samples or lower sensitivities. Only nuclear tracers permit such studies with ease and assurance of what is happening. Tracers often can locate and correct problems in an analytic method in less time than that required to check against an extensive series of carefully prepared standards.

Measurement of radioactive decay offers a simplification of the automation of chemical procedures. Continuous measuring equipment already is available and has been incorporated into operable devices. Simplicity and sensitivity, as well as predictability, push instrumentation toward nuclear measurement techniques.

Two serious problems still prevent nuclear methods from taking their proper place in the analyst's tool kit. The first, training the analyst, is disappearing slowly. More schools are offering courses in nuclear applications as faculty and facilities become available. Many are aimed at the industrial technical man. Short courses in nuclear science have been offered at the American Chemical Society meetings, Atomic Energy Commission facilities, and at universities. Universities with nuclear science programs are injecting a number of informed and capable scientists into technical laboratories across the country.

The second problem is that of public education and acceptance. This problem too, is disappearing slowly. AEC bombards the public with free technical and semitechnical publications, films, and news items. State nuclear agencies also contribute. Public school textbooks, as early as the 5th grade, present peaceful uses of nuclear energy and relate radioactivity to other normal physical phenomena. Nuclear techniques, especially gaging, are becoming commonplace in all areas of manufacture and production.

From these, the average person gets firsthand experience with the application of nuclear energy. With such experience comes the realization tha nuclear energy can benefit man an can be controlled. Technical acceptance is here—public acceptance is no far away. Widespread application mus be near.

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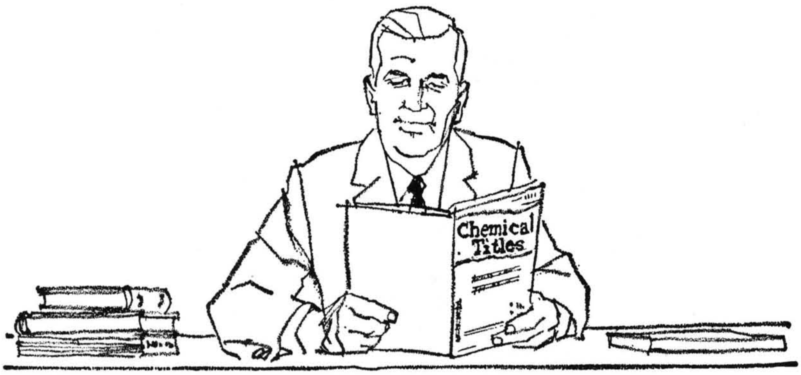
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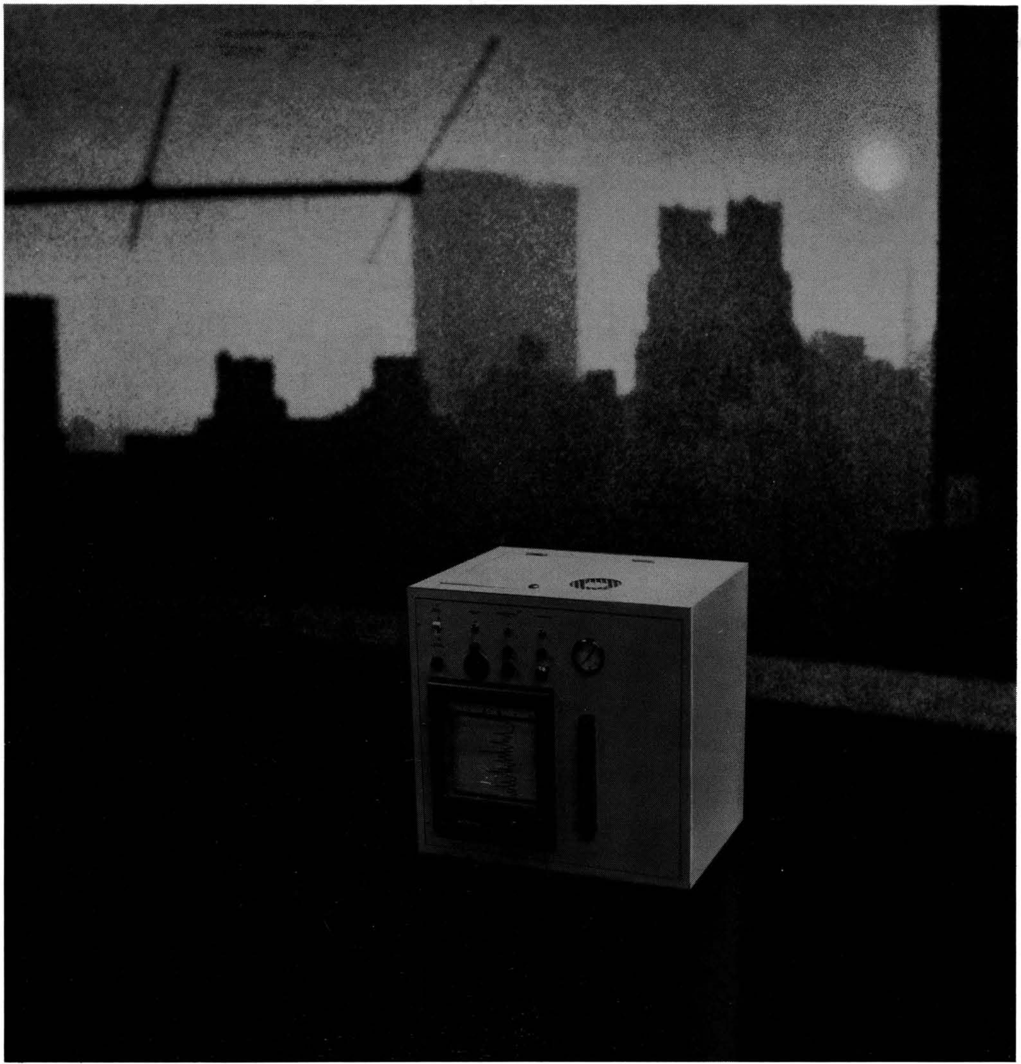

Computational Analysis of Transient Response to Quantitative Shock Loadings of Heterogeneous Populations in Continuous Culture

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■ Heterogeneous populations of sewage origin were grown aerobically on a synthetic waste (glucose as carbon source) in a continuous-flow completely mixed reactor. After establishment of a "steady-state" condition, the system was subjected to a threefold step increase in feed concentration and the transient response was observed. The transient value of cell yield was not constant; the transient values of the specific growth rate constant were not consistent with those predicted by the Monod equation at various substrate concentrations observed during the transient state. Experimental evidence of "growth rate hysteresis" was obtained.

The behavior of microbial populations under various environmental conditions has been of long-standing interest in almost all areas of industrial fermentations. More recently, considerable attention has been given to delineation of the transitional character of continuously cultured systems when subjected to changes in the environment (Eckhoff and Jenkins, 1966; Gaudy, 1962b; Komolrit and Gaudy, 1966a; Krishnan and Gaudy, 1965). This does not belie the importance of characterizing the initial and final steady states (before and after the environmental change), since, for any process, such information is vital for the selection of optimal operational procedures. However, some processes are at times subjected to rather severe environmental pressures, and it is important to know the severity of disruption of the steady state for various types and degrees of external changes (shock loading) which may be imposed upon the system.

Biological processes for treatment of waste waters (in the present instance, the activated sludge process) are perhaps subjected to more severe environmental changes than most other processes, and delineation of the transient response is vital to prediction of the severity and duration of the ensuing disruption of the steady state. Since heterogeneous populations are employed in the treatment of waste waters, the problems of predicting the response are magnified. The type of shock loading considered in the present report, the "quantitative" shock load (Gaudy and Engelbrecht, 1961), consists of a change in the organic loading, in the present case an increase in the concentration of carbon source. Many other types of shock loads are known; however, kinetic analyses and the prediction of the response to these types of shock are representative of more complicated problems than the quantitative shock load. This latter type of environmental change has received the attention of both basic and applied scientists interested in continuous culture growth kinetics.

Methods used for predicting transient performance of continuous cultures (Luedeking and Piret, 1959; Moser, 1957; Northam, 1959) and of the activated sludge process (Eckoff and Jenkins, 1966) are all based upon the Monod equation (Monod, 1949) or some simplification of it.

$$\mu = \mu_m \left[\frac{S}{K_s + S}\right] \tag{1}$$

This expression states the relationship between the specific (logarithmic) growth rate, μ, and the concentration of the growth-limiting nutrient, S. The maximum logarithmic growth rate, μ_m, and the saturation constant, K_s, are assumed to be constants which are characteristic of the system studied—i.e., the cells and the substrate. Natural microbial populations have been shown to perform as predicted by the Monod equation when the carbon source, measured as the chemical oxygen demand (COD), is the growth-limiting nutrient (Gaudy *et al.*, 1967).

The rate of change of biological solids concentration, dX/dt, and the rate of change of substrate concentration, dS/dt, can be given by the equations (Herbert, 1961)

$$\frac{dX}{dt} = \mu(X) - D(X) \tag{2}$$

$$\frac{dS}{dt} = D(S_i) - D(S) - \frac{\mu(X)}{Y} \tag{3}$$

where D is the dilution rate, S_i the substrate concentration in the inflowing feed, and Y the cell yield. Y is defined as the ratio of the rate of solids production due to cell growth to the rate of substrate consumption during growth:

$$\mathrm{Y} = \left(\frac{dX}{dt}\right)_g \bigg/ \left(\frac{dS}{dt}\right)_g \tag{4}$$

The familiar steady-state definition of cell yield is obtained by setting dX/dt and $dS/dt = 0$ in Equations 2 and 3:

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$$Y = \frac{X}{(S_i - S)} \qquad (5)$$

A time-dependent solution of Equations 2 and 3, assuming the cell yield to be constant, has been given by Moser (1957):

$$(S_i - S)(Y) - X = [(S_i - S_o)(Y) - X_o](e^{-Dt}) \qquad (6)$$

where S_o and X_o are the concentrations of substrate and cells at initiation of the transient state—i.e., at time zero.

The value for μ given by the Monod equation may be substituted into Equations 2 and 3, leading to the following expressions for the rate of change of biological solids concentration and rate of change of substrate concentration:

$$\frac{dX}{dt} = \mu_m \left[\frac{S}{K_s + S}\right] X - D(X) \qquad (7)$$

$$\frac{dS}{dt} = D(S_i) - D\,(S) - \mu_m \left[\frac{S}{K_s + S}\right]\left(\frac{1}{Y}\right)(X) \qquad (8)$$

A general solution of the above equations is not possible. A numerical solution was obtained by Northam (1959). Time-dependent solutions have been found by making simplifications of the Monod equation. Luedeking and Piret (1959) obtained a solution by assuming that the substrate concentration was sufficiently high for the specific growth rate to be nearly equal to the maximum specific growth rate. Solutions of Moser (1957) and Eckhoff and Jenkins (1966) were made on the assumption that the substrate concentration is sufficiently low so that the specific growth rate can be approximated by the following equation:

$$\mu = \mu_m \left(\frac{S}{K_s}\right) \qquad (9)$$

Each of these methods for predicting transient performance assumes that the cell yield is constant throughout the transient state.

Concerning the incorporation of the Monod relationship or any modification of it in equations for the transient state, another intrinsic assumption is made. If this relationship—i.e., Monod's—between S and μ is assumed, for each change in S during the transient state there must be an instantaneous change in μ. From a theoretical standpoint, this assumption would not appear to be valid, since it implies instantaneous acclimation to the incremental changes in the environment as S either increases or decreases. Various metabolic control mechanisms governing microbial growth and substrate utilization are well known; various aspects of these mechanisms have been studied in our laboratories, using both heterogeneous populations and pure cultures (Gaudy and Gaudy, 1966). These metabolic regulatory systems for enzyme production and enzyme function not only control the specific enzyme(s) which will be produced, but provide a means of controlling the rate of their production or function, and thus controlling the growth rate. These mechanisms not only provide a means of successfully responding to changes in the environment, but also help to buffer the organisms against such changes.

It is widely accepted that a finite time is required to synthesize the necessary enzyme complement for a particular growth environment. If the concentration of substrate changes, it is reasonable to expect that some time will be required to bring the enzyme complement to a level corresponding to the new substrate concentration in the reactor. Thus, there should be a finite time period wherein μ increases to the level imposed by S upon the system. The change in μ in response to a change in substrate concentration cannot, therefore, be expected to be instantaneous. During the transient state caused by an increase in substrate concentration, μ will not correspond to S, as predicted by the Monod equation, but will be accelerating toward it. Therefore as substrate in the reactor increases, the actual μ observed will be expected to lag behind the μ predicted by the Monod expression. If, on the other hand, substrate concentration is reduced because of an increase in cell concentration subsequent to a step increase in feed, the enzyme levels maintained for the higher S values cannot be expected to be dissipated immediately, and μ observed in the reactor would be expected to lead (or be higher than) the value predicted by the Monod relationship for the instantaneous value of S.

A kinetic theory predicting that for increases in S, μ will be smaller, and for decreases in S, μ will be larger than that expected in accordance with the Monod equation was described originally by Perret, and this deviation was termed "growth rate hysteresis" (Perret, 1960). Based upon the purely metabolic considerations cited above, the occurrence of growth rate hysteresis seems to be an essentially correct and potentially useful postulation. If the growth rate hysteresis phenomenon is manifested in a system during the transient response, it would negate any theoretical validity for use of the Monod equation during the transient state. However, this should not militate against the general applicability of the equation to steady-state situations. As pointed out by Perret, Monod intended the relationship he discovered to apply to the limiting logarithmic growth rate (in both batch and continuous flow systems) and not to the transient growth rate.

Investigational Approach

Various aspects concerning growth and substrate removal in the transient state, due to an increase in substrate concentration, require experimental investigation and analysis. For example, one may pose the question: In view of the postulated phenomenon of growth rate hysteresis, can the Monod expression or any of the previously attempted modifications of it be used to depict the transient response? This question can be approached in two ways. One can establish a biological system in the "steady state" employing an "externally controlled" chemostat (Komolrit and Gaudy, 1966b), then impose an increase in feed concentration and observe changes in the biological solids and substrate concentrations in the reactor (or in the effluent) during attainment (transient state) of the new steady state. To gain an insight into the ability of the Monod relation to describe the transient state, values of the constants μ_m, K_s, and Y may be determined for the system, and using these values in Equations 7 and 8, the corresponding values of X and S may be calculated and compared with the observed values. The values of the constants μ_m, K_s, and Y may be determined in several ways—i.e., from batch data, or from steady-state data (Gaudy, Ramanathan, *et al.*, 1967; Herbert, 1961). Alternatively, with the aid of a computer, one can determine which combination of values for these constants most closely permits a fit of the experimental data. If no combination of reasonable values for these constants can be found which does fit the observed response, it can be concluded that some doubt exists as to the applicability of the relationship for describing the transient state. Another approach would be to test the occurrence of growth rate hysteresis.

In the present study, the approach taken can be described with the aid of the hypothetical response shown in Figure 1. The top graph (1*A*) shows the biological solids concentration,

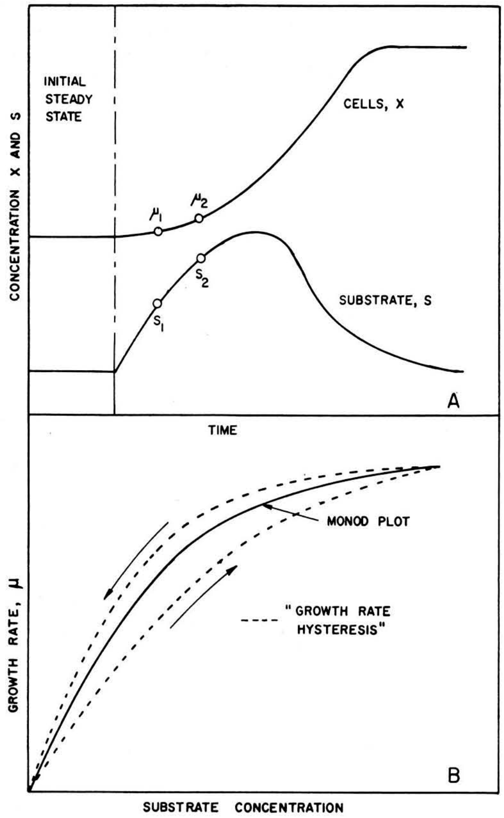

Figure 1. General form of transient response to an increase in substrate concentration, *A*, and relationship between μ and *S* in accordance with the Monod equation and the concept of growth rate hysteresis, *B*

X, and the substrate concentration, *S*, at the start and end of a transient state response to a fairly large increase in concentration of inflowing substrate. The response shown is one in which the substrate removal efficiency is disrupted, the system recovers, and a new steady state is approached. Having previously determined the values of μ_m, K_s, and *Y*, the value of μ at any substrate concentration—e.g., S_1, S_2, etc.—can be calculated in accordance with the Monod equation, and plotted as shown in the solid line curve of Figure 1*B*. On the other hand, one may assume that the transient μ is simply a function of time rather than substrate concentration. The slope of the biological solids curve at any point in time—e.g., at X_1 and X_2, etc., corresponding to S_1 and S_2, etc.—can be determined or approximated, and μ evaluated for comparison with the μ values determined by the Monod relationship. If growth rate hysteresis occurs during the transient, the dotted envelope would be developed—i.e., μ lagging, for increasing values of *S*, and leading, for decreasing values of *S*, the predicted value.

One may also pose the question: Does the cell yield, *Y*, vary during the transient state? A constant *Y* is an intrinsic assumption in all approaches to predicting transient cell and substrate concentrations. There are a number of ways in which the constancy of *Y* may be determined—e.g., *Y* may be calculated from the experimental data during the transient as a function of time and a fit of data using these values of *Y* may be compared to the fit using a *Y* value obtained from the steady-state data or, alternatively, using the constant *Y* of best fit during the transient state. With the above problems in mind, experimental data were obtained for computational analysis.

Experimental Procedures

Heterogeneous microbial populations were developed using an initial seeding of municipal sewage obtained from the primary clarifier of the sewage treatment plant at Stillwater, Okla. The population was maintained in an externally controlled chemostat of the once-through type (Gaudy *et al.*, 1967). The reactor was checked for complete mixing with respect to substrate using the procedures of Komolrit and Gaudy (1966a). Complete mixing with respect to cell concentration was determined daily by checking the equality of cell concentration (absorbance at 540 nm.) in the reactor and in the effluent. The cells in the reactor were completely dispersed and there were no problems due to attachment of cells to the reactor walls. After assessing biological solids concentration and substrate concentration in the initial steady state, the feed concentration was increased while the dilution rate was maintained constant. Samples of the effluent were taken during the resultant transient state, and were analyzed for biological solids concentration and substrate concentration. The sampling was continued until establishment of the new, or final, steady-state condition in the reactor.

In these studies the carbon source (glucose) was maintained as the growth-limiting nutrient. All constituents of the synthetic medium were made up in distilled water, and the concentration of inorganic salts per 1000 mg. per liter of glucose was as follows: $(NH_4)_2SO_4$, 500 mg. per liter; $MgSO_4 \cdot 7H_2O$; 100 mg. per liter; $FeCl_3 \cdot 6H_2O$, 0.50 mg. per liter; $MnSO_4 \cdot H_2O$, 10.0 mg. per liter; $CaCl_2$, 7.50 mg. per liter; KH_2PO_4, 527.0 mg. per liter; K_2HPO_4, 1070.0 mg. per liter; and tap water, 100 ml. per liter.

Biological solids concentration was measured using the membrane filter technique (filter pore size 0.45 micron). Additional biological solids concentration determinations were made by reading the absorbance of the reactor effluent at 540 nanimeters and converting the readings to biological solids concentration using a previously prepared calibration curve. Substrate concentration was measured on the membrane filtrate using the chemical oxygen demand (COD) test (American Public Health Association, 1960). Substrate concentration in the membrane filtrate was also measured using the anthrone test (Gaudy, 1962a). Calculations of the substrate response were based upon values obtained using the COD test, because it provides a measure of the total carbon source and it is a widely used parameter in the water pollution control field.

Computational Procedures

Determination of Transient Values of μ and *Y*, and Subsequent Calculation of *X* and *S*. A plot of the observed concentrations of biological solids, *X*, and substrate, *S* (as measured by the COD test), during the transient state, was divided into small segments—i.e., X_n to X_{n+1} and S_n to S_{n+1}. For the small time period, Δt, of each segment, the specific growth rate, μ, and the yield, *Y*, were assumed to be constant. From the values of *X* and *S* at the initial and final points of this time interval, the values of μ and *Y* were calculated from Equations 10 and 11, which are the integrated forms of Equations 2 and 3 for systems with constant μ and *Y*:

$$\mu = \frac{\ln (X_{n+1}/X_n)}{t} + D \qquad (10)$$

$$Y = \frac{(X_{n+1} - (X_n)e^{-Dt})}{S_i - S_{n+1} - (S_i - S_n)(e^{-Dt})} \qquad (11)$$

To integrate Equation 2 when μ is a variable dependent upon time, it is necessary to express μ as some function of time. To facilitate computations, μ was assumed to be a linear function of time. The value of μ during any time interval during the transient was then approximated by an equation of the form:

$$\mu = a + b(t - f) \qquad (12)$$

a represents the value of μ when t is equal to f (the time of beginning the transient), and b is the slope of the curve approximating transient μ. Substituting the approximated transient μ over this time interval into Equation 2 and solving for the time-dependent state, the value of X at the time t, X_t, may be obtained from the equation:

$$X_t = (X_f)e^{[(a-bf-D)(t-f)+b(t^2-f^2)/2]} \qquad (13)$$

where X_f is the value of X at the initial time, f. In the calculations made for the present study, the time interval Δt or $(t - f)$ was 0.005 hour. This method of determining transient μ and transient X as a function of time is not a means of predicting response, but allows a mathematical reproduction of the response curve and a fairly accurate measure of changes in μ during the transient.

In a similar manner, transient values for Y were approximated using the equation:

$$Y = a' + b'(t - f) \qquad (14)$$

where a' is the value of Y when $t = f$, and b' is the slope of the line approximating transient cell yield, Y. The substrate response can be calculated using a suitable numerical integration technique for Equation 3, incorporating the transient functions for μ and Y. A solution was obtained using the Taylor series expanded to the third derivative—i.e.,

$$S_{n+1} = S_n + \Delta t(S') + \Delta t^2(S''/2!) + \Delta t^3(S'''/3!) \qquad (15)$$

where

S' is as given in Equation 3

$$S'' = -D(S) - X'(\mu/Y) - X(b/Y) + X(\mu)b'/(Y^2) \qquad (16)$$

$$S''' = -D(S'') - X''(\mu/Y) - 2(X') \times (b)(b')/(Y^2) - 2(X)(\mu)(b')b'/(Y^3) \qquad (17)$$

The value of X' used in Equation 17 has been given in Equation 2, and the value of X'' is

$$X'' = (a + bt - D)(X') + b(X) \qquad (18)$$

If the transient values of μ and Y calculated in the above manner can be used to retrace or reproduce the observed substrate response, the values obtained are essentially correct for the system under study.

Determination of Transient Values of X and S Using Monod Equation. Values for the Monod equation constants (μ_m, K_s, and Y) were obtained experimentally for each system under study using methods commonly employed for obtaining the values of these constants. The value of μ_m was obtained from batch experiments at nonlimiting substrate concentrations using cells harvested from the steady-state reactor just prior to administering the increase in feed concentration. The value of K_s was calculated by substituting the initial steady-state substrate concentration and μ_m value in Equation 1, with $\mu = D$. The cell yield, Y, was obtained from the initial steady-state data. To predict the biological solids and substrate concentration during the transient, Equations 7 and 8 were solved using the Taylor series expanded to the third derivative:

$$X''' = \frac{\mu_m}{(K_s + S)} \{X''(S) + 2(X')S' + (X)S'' + [-X'(S')S - X(S')X' - (X)(S)S'' + [X(S)(S')S']/[K_s + S]]/[K_s + S]\} - \frac{\mu_m(S')}{(K_s + S)^2} \{X'(S) + X(S') - [X(S)S'/(K_s + S)]\} - D(X'') \qquad (19)$$

Since Y is taken as a constant, the substrate response can be found by solving Equation 6 for S:

$$S = \{S_i(Y) - X - [(S_i - S_o)(Y) - X_o]e^{-Dt}\} \left(\frac{1}{Y}\right) \qquad (20)$$

After obtaining the value of μ as a function of time (and testing the assumed function for its ability to reproduce the transient biological solids response and its ability in conjunction with the transient values of Y to reproduce the transient substrate response), one can plot these values of the observed μ against values of observed S during the transient state for comparison with the μ predicted by the Monod equation at various values of S observed during the transient state. If an envelope similar to the one shown in Figure 1 is thus developed for the observed values of μ calculated as a function of time, there would appear to be a positive indication of the occurrence of growth rate hysteresis during the transient state.

Results

Six experimental runs were made in which the initial steady state was disrupted by applying a threefold increase in the concentration of carbon source in the inflowing waste. In general, the response patterns which developed were similar. In all cases there was an increase in the biological solids concentration. The biological solids concentration curve approached the new steady-state level along a curve which appeared to describe an autocatalytic increase in all but one case in which an excessive amount of metabolic intermediates and/or end products was produced. In this system the biological solids increased linearly. The expected or typical response (five cases out of six) was an autocatalytic increase in biological solids concentration. The typical response for substrate concentration (filtrate COD) involved, initially, an increase (at a decreasing rate). The substrate concentration passed through a peak and decreased, except for the one experiment cited above, along an S-shaped curve to the final steady state. In four cases there was evidence of the accumulation of metabolic intermediates and/or end products, as judged by comparing the filtrate COD and filtrate carbohydrate (anthrone) concentrations.

The computational approach described earlier was applied to all six sets of data. In all cases, prediction of the transient response using equations incorporating the Monod relationship did not trace or reproduce the transient response with respect to X and S. In only two cases could it be concluded to have provided an acceptable approximation. However, even in these two cases μ did not vary with S in accordance with the Monod equation—i.e., there was evidence of the existence of growth rate hysteresis in the systems. Since the six experimental runs gave essentially the same response, the observed experimental results and results using the computational procedures outlined previously are presented for one of these experiments, in which there was evidence for the accumulation and subsequent utilization of organic metabolic products produced in response to the increased glucose concentration in the inflow.

Figures 2 and 3 show the observed and computed responses with respect to biological solids concentration and substrate concentration. For this experiment, the feed concentration in the initial steady state was 450 mg. per liter COD. At time zero, the feed concentration was changed to 1450 mg. per liter COD. The biological solids and substrate concentrations in the reactor at the initial steady-state condition (X_o and S_o) were, respectively, 230 and 90 mg. per liter. The response curves calculated on the assumption that μ and Y are functions of time, in accordance with the methods outlined pre-

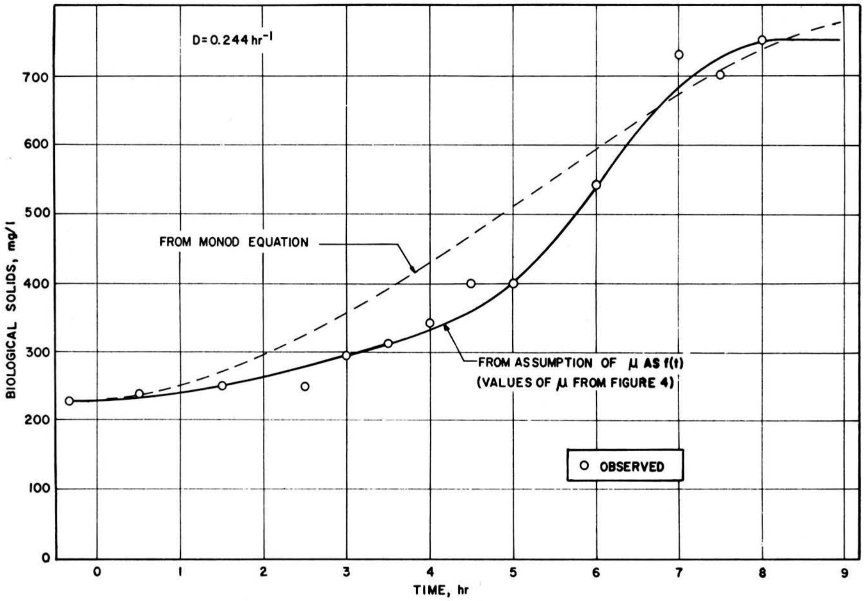

Figure 2. Transient biological solids concentration in response to an increase in concentration of growth-limiting nutrient

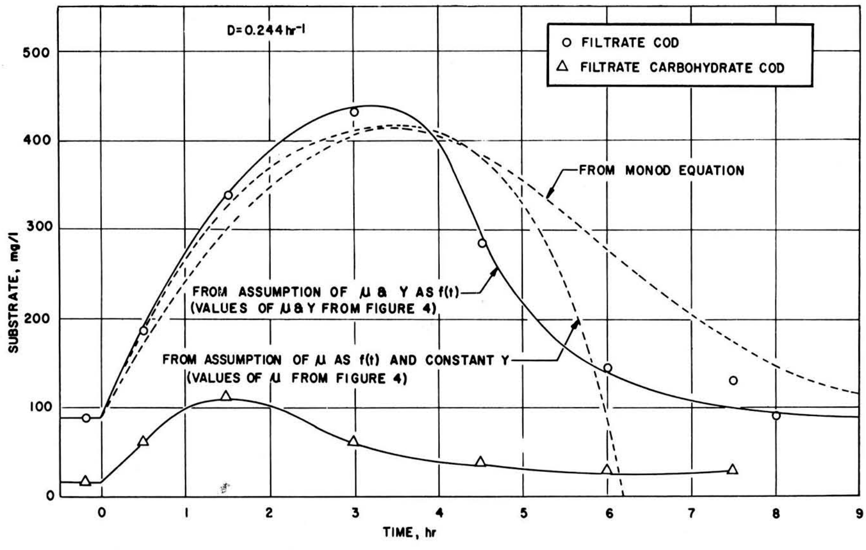

Figure 3. Observed and calculated transient substrate concentration in response to an increase in concentration of growth-limiting nutrient

viously, fitted the observed data for solids and substrate well.

The Monod equation constants, calculated from the data in accordance with the methods previously described, were: $\mu_m = 0.54\ \text{hour}^{-1}$, $K_s = 106$ mg. per liter, $Y = 0.64$. Numerical integration of the transient state equations employing these constants yielded the predicted responses shown in Figures 2 and 3. This procedure, which represents a means of predicting the transient response, since it does not require use of observed transient data, provided a rough approximation of the response.

Figure 3 shows the predicted transient substrate response using μ as a function of time, and assuming yield to be constant. Several values of Y were tried to find the value which gave the best agreement with the observed substrate response. Of the values tried, $Y = 0.46$ gave the best fit, and the response shown is one obtained using this value. Also shown in Figure 3 is the observed response with respect to carbohydrate COD. This response was obtained using the anthrone test and converting the results to their equivalent COD values—i.e., carbohydrate COD = 192/180 × carbohydrate measured by the anthrone test. A considerable amount of metabolic intermediates and/or end products was accumulated and subsequently metabolized during the transient state.

The transient μ and Y values, calculated from the observed biological solids and substrate concentrations as a function of time during the transient, are shown in Figure 4. The calculated biological solids and substrate responses of Figures 2 and 3 were made using these transient values of μ and Y.

The cell yield prior to administering the increase in feed concentration was 0.64. Figure 4 shows that the initial response was a large immediate increase in Y, calculated as $(dX/dt)_g/(dS/dt)_g$, accompanied by a rapid increase in μ—that is, there was a small initial increase in biological solids concentration during this period (Figure 2) although the substrate removal rate increased only slightly, since the increase in S was very close to that expected from the calculated theoretical "dilute-in" curve for substrate. This effect was noted in five of the six experiments, and it may indicate a rapid uptake of carbon into storage products.

During the first 30 minutes, Y decreased to approximately 0.5, and μ dropped to slightly under 0.3. Thereafter, during the period of maximum COD leakage—i.e., until approximately 4 hours after administering the shock (Figure 3)—μ increased slightly, and Y decreased in a stepwise fashion. Thereafter both parameters increased linearly, as the system recovered its efficiency of carbon source removal, reached peak values at approximately 6 hours, and then returned to their former steady-state values.

The data obtained do not explain the stepwise changes in μ and Y before the response picked up momentum—i.e., during the first 4 hours or the period of increasing COD leakage. However, Figure 3 shows that a considerable amount of the COD appearing in the effluent was noncarbohydrate in nature; thus, there was ample evidence that compounds other than the original carbon source, glucose, were produced during this period. The stepwise changes in μ and Y may be due to metabolism of various organic compounds elaborated by the cell population. The peak in the transient μ curve (approximately 6 hours, Figure 4) was attained after the peak in effluent substrate (approximately 3 hours, Figure 3).

In Figure 5 the values of μ predicted by the Monod relationship, Equation 1, at the various values for filtrate COD observed during the transient (Figure 3) are compared with the values taken from Figure 4 at the times corresponding to the filtrate COD values taken from Figure 3. During the period of increasing COD concentration, the transient μ values are lower than those predicted by the Monod equation. Also, as the substrate concentration decreases, the transient μ values are higher. A similar trend was observed for the other systems investigated. The results provide experimental evidence for the occurrence of "growth rate hysteresis," as postulated by Perret (1960).

Discussion and Conclusions

The transient state biological solids and substrate concentrations subsequent to an increase in inflowing waste concentration cannot be predicted with accuracy by employing the Monod equation. One of the underlying reasons for the inability to predict the transient response is the variation of the cell yield, Y, during the transient state. Of even greater significance is the experimental demonstration of growth rate hysteresis, the occurrence of which makes it theoretically impossible to use the Monod relationship, since instantaneous response of μ to changes in S would be required.

In the present work, the cell yield was calculated as the ratio of the instantaneous rate of production of biological solids (dX/dt) to the rate of COD utilization (dS/dt), using Equation 4 rather than employing the usual steady-state procedure—i.e., calculation of Y as $X/(S_i - S)$ (Equation 5), which represents a special case applicable only in the steady state. COD values were used in preference to the anthrone values for reasons outlined previously, and because in many cases there was evidence for the production and accumulation, in the medium, of metabolic intermediates and/or end prod-

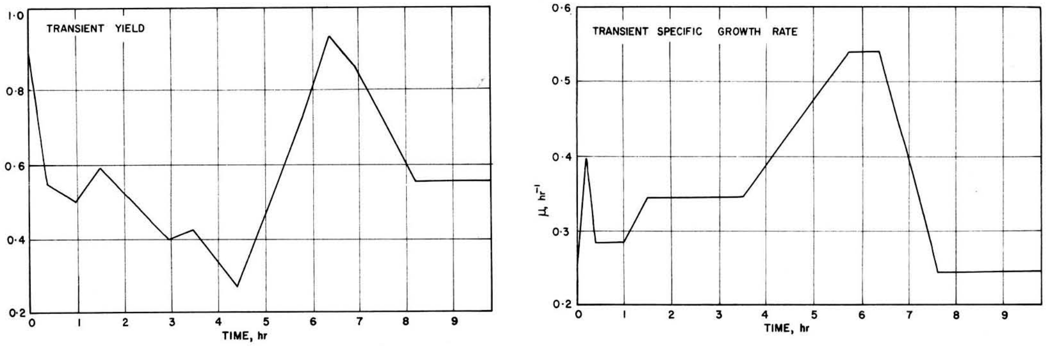

Figure 4. Changes in values of μ and Y, calculated as a function of time, during transient response shown in Figures 2 and 3

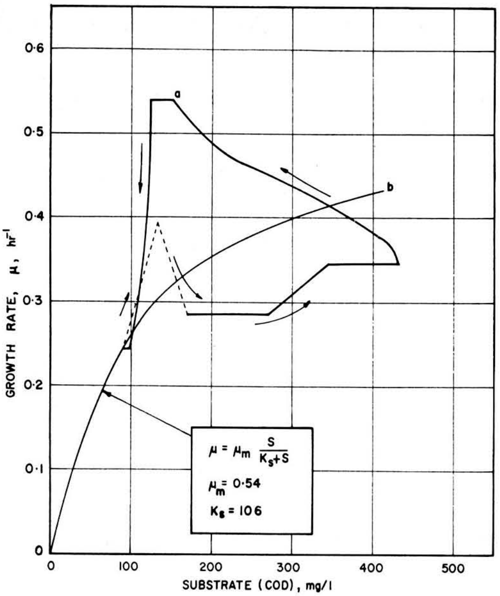

Figure 5. Values of μ *vs.* S for observed data calculated with μ as a function of time, *a*, and μ as a function of S in accordance with the Monod equation, *b*

ucts during the metabolism of the initial carbohydrate (glucose) fed into the aerator. Once produced, these soluble organic products of metabolism became substrates which were available to the cells, and were subsequently metabolized. Thus, from the standpoint of reducing the pollutional potential, it seemed valid to use this parameter (COD) as a measure of S. Part of the variation in Y may be attributable to the fact that the chemical structure of S was changed because of the metabolic activity of the feeding population. However, the value of Y, during the transient state, varied (although not to as great an extent) for the systems in which the accumulation of organic metabolic products was not evident. This phenomenon (production and subsequent utilization of metabolic products), observed in other studies (Krishnan and Gaudy, 1965), is significant in that it is not one which is observed only in heterogeneous populations (Clifton, 1963; Gaudy and Gaudy, 1966).

The purpose of using heterogeneous populations in these studies was (as with the use of the COD test) to determine whether kinetic theory developed without this complicating factor could be employed in the pollution control field. In this field, engineering economy dictates the use of natural populations, and the nature of the wastes precludes the sole use of a specific substrate analysis, since very few waste waters consist of "sole" sources of carbon. With pure cultures as well as with heterogeneous populations the cells can create a mixed substrate system from a single carbon source. Also, the fact that growth rate hysteresis could be demonstrated for heterogeneous populations provided, in some respects, a more positive indication of its occurrence than if the same phenomenon had been observed using a pure culture. The irregularities in the envelope may be due in part to both the heterogeneity of the population and the presence of carbon sources other than the original one. From the standpoint of studying the basic kinetic aspects of growth rate hysteresis and its effect on the transient performance of a system, it would be well to pursue further work using a sole carbon source and a pure culture which did not elaborate organic metabolites during metabolism of the carbon source. Such a system would provide, perhaps, the most simple model for basic studies.

Although the results of the present study indicate that the relationship between μ and S as depicted in the Monod equation cannot be employed to describe the transient performance with respect to cell and COD concentration, it can be seen in Figure 3 that the Monod equation did predict fairly well (with the additional assumption of constant Y) the maximum COD concentration in the effluent during the transient state (slightly in excess of 400 mg. per liter). Thus it might be concluded that it has at least a limited utility. Also, in the present study a threefold increase in inflowing substrate concentration was employed. For smaller increases in substrate concentration, the growth rate hysteresis phenomenon may not be so prominently manifested.

The results indicate that in future work a dual approach to the problem could provide very useful information. Basic studies using pure cultures with relatively uncomplicated metabolic growth patterns—e.g., absence of organic metabolic products in the medium during transient—to determine the kinetic properties affecting the course of growth rate hysteresis should provide information upon which to base quantitative kinetic statements concerning the phenomenon. Such studies may lead to establishment of kinetic theory upon which to base prediction of transient response. Studies of a more practical nature employing both pure cultures and heterogeneous microbial populations to determine whether generalized transient responses, with respect to biological solids and substrate concentrations, emerge under a variety of controlled environmental changes would provide useful guidelines for immediate application to the control of natural populations—e.g., control of biological waste water treatment facilities.

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Identification and Differentiation of Heavy Residual Oil and Asphalt Pollutants in Surface Waters by Comparative Ratios of Infrared Absorbances

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■ To determine the chemical nature of the heavy petroleum products involved in the 1967 Lake Michigan oil spill, a procedure for the characterization and identification of the oily, tarlike materials was needed. Samples from beach water were analyzed by infrared spectrophotometry. The unknown spectra could not be matched with the known spectra, since autoxidation caused changes in the unknown specimen. By comparative ratios of infrared absorbances, the identity of the critical unknown samples was established. Even though asphalt and heavy residual oil have similar infrared spectra, there is a sharp distinction. Samples from seven petroleum companies were tested, using this new method for rapid characterization.

The 1967 Lake Michigan oil spill (Johnson *et al.*, 1968) ruined long stretches of natural recreational facilities in Chicago, contributed taste and odor problems to potable water, and imposed a large cost in human effort and economic resources. To determine the chemical nature of the heavy petroleum products involved, procedures for the rapid characterization and identification of these oily, tarlike materials were needed. No literature information is available on analytical methods for differentiating asphalt from heavy residual oil, known as No. 6 fuel oil, nor is there a suitable procedure for the characterization of heavy residual oil.

The identification of asphalt is considered extremely difficult. Havens and Daniels (1956) show that asphaltic materials have numerous variations in physical properties and in the extent of oxidation. By infrared spectroscopic studies, Beitchman (1959) and Campbell and Wright (1966) have contributed to the knowledge of asphalt and its oxidative changes. To show that the nature of the hydrocarbon structure of an asphalt has a major effect upon its weatherability, Smith *et al.* (1966) applied quantitative infrared spectroscopic techniques to coating asphalts. They classified asphalts according to the geographical-producing areas, by plotting the ratio of the intensity of the methylene rock absorption at 720 cm.$^{-1}$ to the intensity of the carbon methyl absorption at 1375 cm.$^{-1}$ against the intensity of the aliphatic C—H peak at 2924 cm.$^{-1}$

Bhattacharya (1959) classified the nature of lubricating oils. He proposed the ratio of band areas at frequencies 1600 and 720 cm.$^{-1}$ as a measure of the aromatic or paraffinic character of crude oils. The main variable between some domestic and foreign residual fuels is in the amount of straight-run and cracked components. Domestic fuels are generally mixtures of catalytically cracked, thermally cracked, and straight-run residues, while foreign residual fuels contain predominantly straight-run products.

By use of several infrared wave number ratios, the asphalts and the residual oils may be classified separately and distinctly. The method of comparative ratios of infrared intensities is a new and rapid technique to identify residual oils and differentiate them from asphaltic materials.

The objective was to develop a suitable analytical procedure that would permit rapid characterization and identification of heavy residual oil and to distinguish the residual oil from the asphalt in a mixture, since asphalt and oil can coexist as pollutants on surface waters.

Experimental

Although conditions of samples varied, all were extracted with redistilled, analytical grade chloroform, and the extract was then filtered through anhydrous, reagent grade sodium sulfate.

The concentrate was evaporated by means of an infrared heat lamp (Brown *et al.*, 1967). Exposure was limited to fewer than 10 minutes at temperatures well below 100°C.

Samples for infrared analysis were dissolved in chloroform, and thin rock salt smears were prepared. All remnants of solvent were removed with aid of the infrared heat lamp prior to analysis.

Specimens of unknown pollutants from the Lake Michigan oil spill and known commercial products were analyzed with the Perkin-Elmer 137 Infracord spectrophotometer, operated at slow-scan speed with a slit opening of 25 mm.

Absorbances were determined by the base-line technique. The length of the vertical line, which intersects the line tangential to the two proximate inflections, was measured. Ratios of intensity of the infrared absorption at one frequency to that at another frequency were considered in order to find a discriminating and characteristic property for the residual oil and for the asphalt.

Discussion

The data reported in Table I show that these infrared absorbance ratios (R.I.A.) provide a means of distinguishing residual oils from asphaltic material, since these petroleum products possess strong characterization factors, such as aromaticity and paraffinicity.

Four typical spectra, initially studied and interpreted on the basis of these ratios of infrared absorbances, are shown

Table I. Ratios of Infrared Absorbances

R.I.A.	No. 740 Residual Oil	No. 739 Asphalt	Unknowns No. 730	Unknowns No. 742	Unknowns No. 721
$\frac{720\ \text{cm.}^{-1}}{1375\ \text{cm.}^{-1}}$	0.21	0.30	0.29	0.32	0.38
$\frac{3050\ \text{cm.}^{-1}}{2925\ \text{cm.}^{-1}}$	0.32	0.16	0.12	0.15	0.08
$\frac{810\ \text{cm.}^{-1}}{1375\ \text{cm.}^{-1}}$	0.43	0.25	0.25	0.23	0.13
$\frac{810\ \text{cm.}^{-1}}{720\ \text{cm.}^{-1}}$	2.00	0.80	0.84	0.71	0.35
$\frac{1600\ \text{cm.}^{-1}}{1375\ \text{cm.}^{-1}}$	0.57	0.48	0.50	0.46	0.35

(Figure 1) of the following samples: a known heavy residual No. 6 oil designated as No. 740; a known asphalt sample, No. 739; an unknown Chicago beach petroleum pollutant sample, No. 730; and an unknown sample, No. 721, which was retrieved in a harbor canal.

The No. 739 asphalt spectrum shows the usual hydrocarbon absorption bands at 2925, 2849, 1455, and 1375 cm.$^{-1}$ In addition to these bands, aromatic absorption is designated by the peaks at 869, 810, 745, and 1600 cm.$^{-1}$ Also, long-chain methylenic paraffinicity was specified by the 720-cm.$^{-1}$ peak, whereas only traces of olefinic groups were indicated.

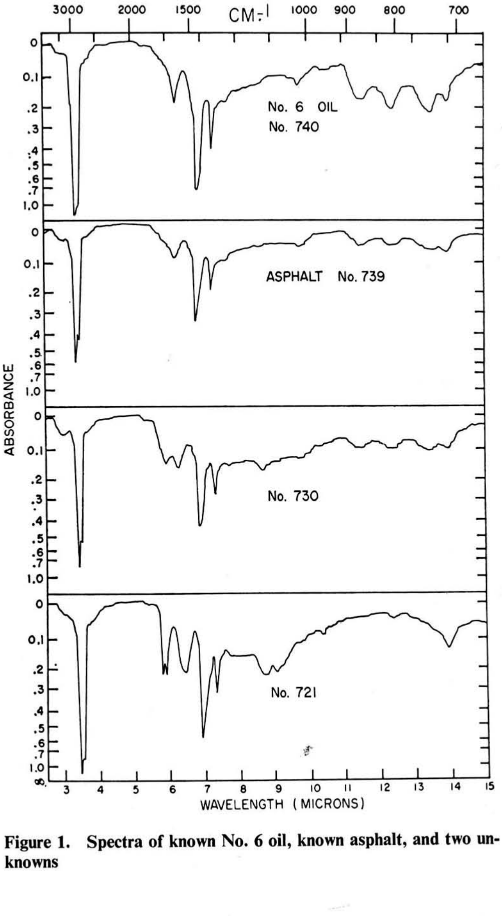

Figure 1. Spectra of known No. 6 oil, known asphalt, and two unknowns

The known No. 6 oil designated as No. 740 displays the usual aliphatic and aromatic absorption bands. Thus, the asphalt spectrum appears to be the qualitative likeness of the residual oil spectrum. The asphalt can be differentiated from the residual oil by comparing the amount of aromatics that cause the designated absorptions, relative to the aliphatic nature of each petroleum product. The last four values for residual oil in the first column in Table I reflect a larger specific aromatic content when these aromatic-aliphatic ratios are compared to the numbers in the column for asphalt 739. The No. 740 residual oil shows a higher ratio of aromatic CH absorbance at 3050 cm.$^{-1}$ to the methylene asymmetric stretch vibration, 2925 cm.$^{-1}$ A predominant feature of the No. 740 residual oil is the high content of aromatic rings that cause absorption at 810 cm.$^{-1}$

Asphalt material No. 739 shows not only relatively less absorption at 810 cm.$^{-1}$ but relatively stronger absorption at 720 cm.$^{-1}$ The only comparative ratio for which the asphalt is greater is the ratio of the 720-cm.$^{-1}$ chain methylene rock vibration, to the 1375-cm.$^{-1}$ C—CH$_3$ branching. Therefore, with the exception of the fifth ratio, the comparative ratios of infrared absorbances are distinctive and are distinguishable for these two types of petroleum products.

Of the two unknown spectra assessed, No. 730 is similar, qualitatively, to the No. 739 asphalt. The qualitative differences in the spectra of Nos. 730 and 739 exist mainly with absorption peaks at 1695 and 1150 cm.$^{-1}$ for the No. 730 spectra. These absorption peaks illustrate the effects of the oxidation process upon the originally known asphalt material No. 739. Carbonyl groups and, possibly, ether groups are present in unknown 730. Ethers (Kawahara, 1957, 1965) are formed as secondary products during the autoxidation of highly reactive olefins. Presumably, an alkoxy free radical attack upon conjugated diolefin, followed by stabilization of the free radical via hydrogen abstraction, results in ether formation. Since the known asphalt material may contain traces of conjugated olefins as indicated by an inflection at 1640 cm.$^{-1}$ in No. 739, the facile peroxidation of the asphalt, when diluted with some residual oil, will promote formation of carbonyls and ether groups. Otherwise, spectra of unknown No. 730 are similar to No. 739 asphalt, as attested by the close quantitative agreement of their ratios of infrared absorbances. Of the five comparative ratios, four are alike. The presence of the diluent No. 6 oil cannot be discounted, as these variances in the ratios suggest dilution of asphalt.

A possible explanation for the presence of the 1025-cm.$^{-1}$ absorption peak in No. 739, the known asphalt; for its subsequent absorption decrease in No. 730, the unknown asphalt; and for the appearance of the absorption peaks at 1155 and 1295 cm.$^{-1}$ in the unknown is the conversion of sulfoxides of the known asphalt to the sulfones, which absorb at 1155- and 1295-cm.$^{-1}$ bands in the unknown asphalt. This oxidation (Stewart, 1957) would further strengthen the autoxidation thesis of the asphaltic residual oil materials in water, especially when the asphalt is mixed with the residual oil. Residual oils are composed of "cracked" material.

Unknown sample 721 is faintly similar to the first three spectra. The aromatic absorption is much less, as shown by the last four ratios of the last column. Two carbonyl bands are present at 1725 and 1696 cm.$^{-1}$ Absorption at 1110 cm.$^{-1}$ indicates an ether group. The ratio of the methylene rock vibration to the carbon methyl deformation frequency is

Table II. Ratios of Infrared Absorbances

R.I.A.	No. 6 Residual Oil	Asphalt	Unknowns			
			No. 702	No. 724	No. 734	No. 832
$\frac{720 \text{ cm.}^{-1}}{1375 \text{ cm.}^{-1}}$	0.21	0.30	0.10	0.26	0.23	0.30
$\frac{3050 \text{ cm.}^{-1}}{2960 \text{ cm.}^{-1}}$	0.32	0.16	0.05	0.06	0.06	0.24
$\frac{810 \text{ cm.}^{-1}}{1375 \text{ cm.}^{-1}}$	0.43	0.25	0.18	0.26	0.27	0.24
$\frac{810 \text{ cm.}^{-1}}{720 \text{ cm.}^{-1}}$	2.00	0.80	1.71	1.00	1.16	0.80
$\frac{1600 \text{ cm.}^{-1}}{1375 \text{ cm.}^{-1}}$	0.57	0.48	0.18	0.45	0.50	0.36

large, suggesting a strong paraffinic nature of the pollutant admixed with the No. 6 oil and the asphaltic material.

Other oil pollution samples retrieved during the spills were subjected to the new method of identification. In Table II are the ratios of the samples considered in addition to No. 742 found in Table I.

Inspection of spectra 724, 734, 742, and 832 shows that many of the paraffinic and aromatic band absorptions are also common to unknown 730 and known asphalt 739. Sample 702 differs in appearance from the No. 739 spectra; the values of ratios vary widely from the ratios of the infrared absorbances of known asphalt 739 (Figure 2).

Inspection of the values under Nos. 742 and 832 reflects comparative ratios similar to asphalt or No. 739. Indeed, the infrared spectra of Nos. 742, 832, and 739 asphalt, and No. 740 residual oil are similar.

By comparing ratios of $\frac{810 \text{ cm.}^{-1}}{720 \text{ cm.}^{-1}}$ and $\frac{810 \text{ cm.}^{-1}}{1375 \text{ cm.}^{-1}}$ from Nos. 742, 832, 739, and 740, samples 742 and 832 are found to be quantitatively similar to No. 739 asphalt. These two ratios reflect the distinctive difference between residual oil and asphalt in the relative amount of the structure of two to three adjacent hydrogens on an aromatic ring which cause absorption at 810 cm.$^{-1}$ Inspection of ratios of 810 to 1375 cm.$^{-1}$ and 810 to 720 cm.$^{-1}$ shows samples 724 and 734 to be more like asphalt 739. Although the infrared spectra of these two unknowns are qualitatively similar to asphalt 739 and to residual oil 740, the two are distinguishable by comparing the ratios of intensities of the out-of-plane bending vibrations to the C—CH_3 bending or to chain methylene rock vibrations. The two smaller ratios of Nos. 724 and 734 are characteristic of the asphalt material.

The usefulness of this classification method was confirmed by examining other commercially available products. Figure 3 illustrates the four spectra. Qualitatively, they are similar.

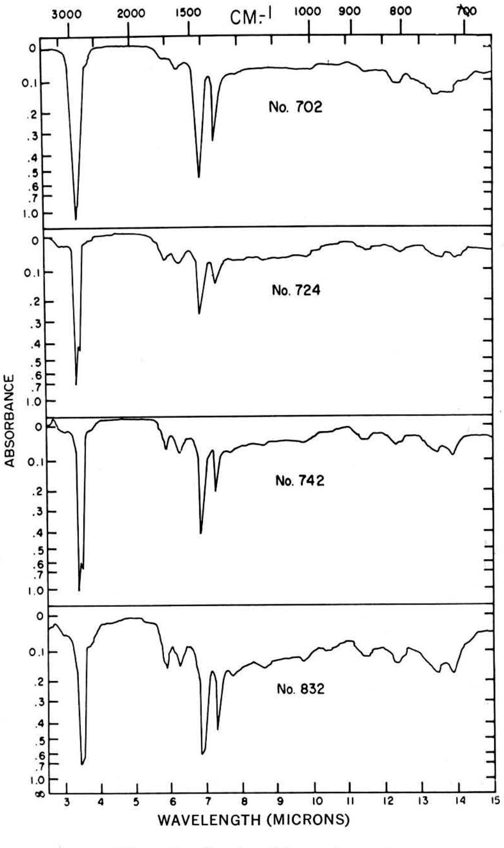

Figure 2. Spectra of four unknowns

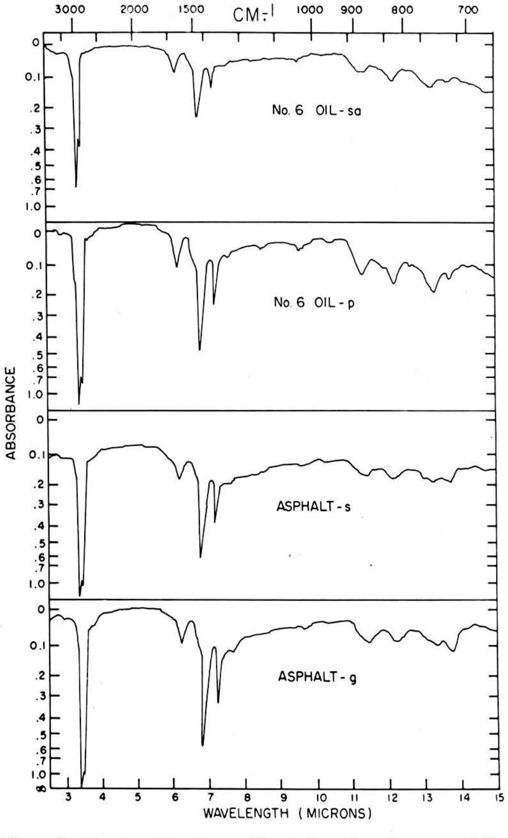

Figure 3. Spectra of two known No. 6 oils and two known asphalts

Table III. Ratios of Infrared Absorbances of Commercial Products

R.I.A.	Asphalt			No. 6 Oil				
	g	si	s	s	p	b	s	si
$\frac{720 \text{ cm.}^{-1}}{1375 \text{ cm.}^{-1}}$	0.30	0.30	0.23	0.16	0.16	0.18	0.16	0.21
$\frac{3050 \text{ cm.}^{-1}}{2925 \text{ cm.}^{-1}}$	0.18	0.16	0.18	0.20	0.26	0.27	0.28	0.32
$\frac{810 \text{ cm.}^{-1}}{1375 \text{ cm. }^{1}}$	0.20	0.25	0.23	0.58	0.52	0.45	0.59	0.43
$\frac{810 \text{ cm.}^{-1}}{720 \text{ cm. }^{1}}$	0.67	0.80	1.00	3.50	3.20	2.50	3.67	2.00
$\frac{1600 \text{ cm.}^{-1}}{1375 \text{ cm.}^{-1}}$	0.47	0.48	0.55	1.00	0.75	0.68	0.97	0.57
$\frac{1600 \text{ cm.}^{-1}}{720 \text{ cm.}^{-1}}$	1.55	2.16	1.83	6.00	4.75	4.00	6.00	3.16

Ratios of the infrared absorbances of products from different sources are given in Table III.

Inspection of data bears out the two key ratios which distinguish asphalt from residual oil: the intensity of the 810-cm.$^{-1}$ absorption to the intensity of the 1375-cm.$^{-1}$ absorption and intensity of the 810-cm.$^{-1}$ absorption to the intensity of the 720-cm.$^{-1}$ absorption.

Values of these ratios for asphalt are about one half those for the residual oil. Thus, the asphalt material, compared to the residual oil, shows fewer aromatics of the types that cause absorption at 810-cm.$^{-1}$ Figure 4 shows the sharp distinction of the aromatic to aliphatic ratios of infrared absorption values for the asphalts and for the residual oils obtained from seven oil companies.

Located near the origin in contrast to the heavy residual oil points are the asphalt points, most of which fall on the common line expressed by the equation $y = 0.13x + 0.125$.

The positive slope denotes proportional decrease of aromatics responsible for absorption at 810 cm.$^{-1}$ for points located near the origin. In contrast to residual oils, asphalts are characterized by relatively larger intensities caused by carbon methyl and methylene chains. For both asphalt and heavy residual oil, the absorption due to carbon methyl branching is about four times that due to the methylene chains.

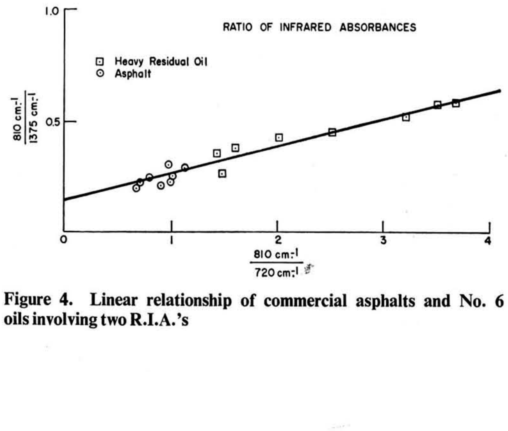

Figure 4. **Linear relationship of commercial asphalts and No. 6 oils involving two R.I.A.'s**

Table IV. Effect of Exposure of No. 6 Residual Oil to Air at 23° C.

Exposure Time, Days	Ratio of Intensities			
	$\frac{1030 \text{ cm.}^{-1}}{1375 \text{ cm.}^{-1}}$	$\frac{1155 \text{ cm.}^{-1}}{1375 \text{ cm.}^{-1}}$	$\frac{1300 \text{ cm.}^{-1}}{1375 \text{ cm.}^{-1}}$	$\frac{1695 \text{ cm.}^{-1}}{1375 \text{ cm.}^{-1}}$
1	0.113	0.065	0.065	0.23
8	0.196	0.072	0.079	0.25

To determine whether the heavy residual oil could autoxidize rapidly, a small portion of this oil was exposed to air at ambient conditions for 8 days. Examination by infrared spectrophotometry indicated facile formation of sulfoxides from thioethers. Table IV shows the strong increase of the 1025- to 1375-cm.$^{-1}$ ratio obtained after the heavy residual oil was exposed to air. This increase may be due to either the oxidation of the thioether to sulfoxide or the formation of aryl and alkyl ethers. The conversion of sulfoxides to sulfones and/or the formation of alkyl ethers and secondary alcohol are probably indicated by the small increases of the 1155- to 1375-cm.$^{-1}$ and the 1300- to 1375-cm.$^{-1}$ ratios. A small increase is noted for the ratio of carbonyl to the carbon methyl.

These results present strong evidence as to the usefulness of this new and much needed, rapid method for distinguishing the two types of petroleum products which can coexist in surface waters as pollutants.

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A New Instrument for the Evaluation of Environmental Aerocolloids

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■ A single-stage, multiple-slit impactor was designed to precipitate aerocolloidal particles in the submicron range ($d \geq 0.2$ micron) on the metallic mirror surface of a slide, which moves perpendicular to two to four equal slit exits. This motion can be varied in exponential intervals over a range of 1 to 512 to obtain a sequence of deposit steps with uniform but varying density. Coagulation and mutual interference, inevitable in most other impaction processes, are avoided by control of the deposit density with the slide speed which is reproducible by synchronous drive. To determine the critical concentration at which coalescence occurs, a series of steplike deposits from each slit exit varying exponentially in density permits the correlation of particle number with air volume in the range of 10^0 to 10^6 per liter. The deposit density is determined by measuring the light-scattering levels microphotometrically under reflected dark-field illumination. The multiple-slit arrangement facilitates comparison of deposits from different branches of the same air sample, prior to impaction exposed to high humidity, infrared, or ultraviolet irradiation, and indicates the hygroscopic, thermal, and photochemical stability of the prevailing aerocolloids.

The purpose of the moving slide impactor (MSI) is rapid evaluation of locally prevailing levels of aerocolloidal matter—i.e., aerosol particles predominantly in the submicron range—and survey of the liquid or solid constitution, hygroscopic properties, and thermal and chemical stability of these particles. While the data obtained with the MSI, unlike the cascade impactors and the aerosol spectrometer (Goetz, 1957; Goetz and Kallai, 1964; Goetz *et al.*, 1960), do not reveal the size distribution of the particles, they approximate the degree of visibility restriction to be expected from the aerocolloidal matter in the air sample.

A moving, rather than a stationary, impaction surface is used to avoid the areal inhomogeneity of the deposits, particularly at prolonged exposures, due to the steep variation of the flow velocity across the slit exit. Impaction on moving surfaces has been applied by several authors, on paper strips, rotating cylinders, and microslides, particularly for identification of specific particle types, such as spores (Hirst, 1952), but also for producing reactions between particles and sensors on the impacted surface (Goetz and Tsuneishi, 1959), and on a four-stage cascade-impactor (May, 1956) (Casella-type) with moving slides at each stage in the particle size range (5 to 50 microns).

However, these designs are not applicable to the permanently airborne aerocolloidal matter, which presents by order of magnitude ($\sim 10^{-6}$) lesser individual particle masses and very much larger frequencies.

The MSI developed for this specific purpose differs in many aspects. It is a single-stage, multiple-slit impactor, which deposits the particles on the metallic mirror surface of a microslide. The slide moves beneath the slits at variable velocities, so that the simultaneously impacted deposits from each slit unit cover equal separate areas on the slide. The velocity of the slide motion relative to the slit apertures can be varied in exponential progression and controls the deposit density. The availability of different densities facilitates the assay of the prevailing aerosol levels and determination of the "critical" density at which coalescence occurs. A sequence of deposit densities in the form of rectangular steps is produced when the slide velocity is doubled between adjacent steps; a density ratio exceeding 500 can be covered by up to 10 steps.

The advantage of step deposits over continuous density variation is the availability of a uniform area, large enough to permit repeated micro-optical evaluation at different locations on the same density level, thus minimizing statistical fluctuation. The reason for the exponential step order is the convenience of graphic evaluation on semilog diagrams, where the data of the sensor must follow straight lines of defined slope, independent of the optical qualities of the prevailing particles, until the critical deposit density is reached.

Besides subdividing the deposit into individual steps, the slide can also be moved continuously at any one of 10 available speeds. This results in a "plateau" deposit, which records variations of aerosol density during time intervals between 1 minute and $8\frac{1}{2}$ hours. Figure 1 presents typical slide deposits produced in this manner.

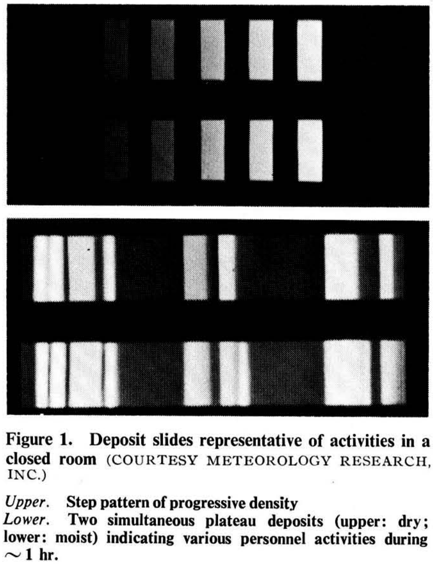

Figure 1. Deposit slides representative of activities in a closed room (COURTESY METEOROLOGY RESEARCH, INC.)

Upper. **Step pattern of progressive density**
Lower. **Two simultaneous plateau deposits (upper: dry; lower: moist) indicating various personnel activities during $\sim$1 hr.**

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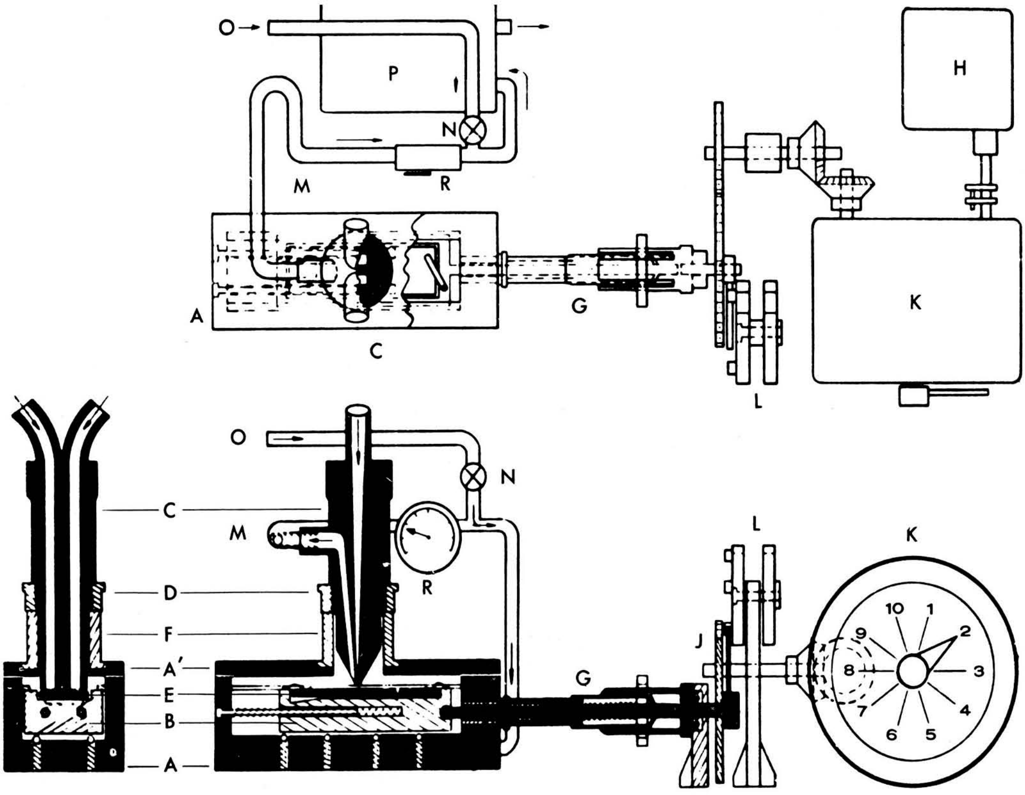

Figure 2. Moving slide impactor

Upper. **Schematic top view**
Lower. **Vertical cross sections**

The multiple slit system consists of two or four geometrically identical units which produce separate deposits of the same air sample simultaneously. This permits evaluation of the hygroscopicity, thermal and photochemical stability, etc., of the prevailing aerocolloidal matter when different branches of the same air flow, before entering the impactor, are briefly exposed to specific conditions, such as elevated humidity, temperature, and irradiation, for subsequent comparison of the corresponding deposit patterns.

Design and Operation

The basic construction of the impactor is shown in Figure 2. The space where impaction occurs is confined to the heavy, rectangular aluminum case, *A*, covered by a hinged lid, *A'*, which is vacuum-sealed to *A* during operation. The slit unit, *C*, is an integral part of *A'*. The carrier, *B*, which contains the impaction slide, *E*, in a fixed position moves horizontally within *A* and is held by spring rollers against the upper edge of *A* so as to maintain an exactly defined distance from the slit exits of unit *C*.

The impaction slide, *E*, consists of a highly polished metal plate or glass slide (25 × 75 mm.) with a Cr-Ni surface mirror, protected by a SiO layer. It fits into a recess on *B* and is held there by spring clamps which provide an electric contact between the surface of *E* and the instrument body. Besides avoiding the formation of electric surface charges on *E*, this contact provides for a sensitive adjustment of its critical distance from the slit exists. The metal body of *C* is attached to *A'* by a nonconducting socket, *F*, wherein the vertical position of *C* can be adjusted within ±0.025 mm. by the micrometer unit, *D*. An electric circuit connects a 6-volt dry cell with *C* and *A* in series with a pilot light (not shown in Figure 2), which signals whenever the slits, lowered by *D*, touch the slide surface. Thereafter *C* is lifted to the optimal distance, indicated by the scale on *D*. The distance adjustment is independent of the slide thickness.

C is exchangeably mounted in *A'* and contains either two or four separate, identical slit channels, where the slit lengths are twice as large in the twin as in the quadruple units. The *C* unit connects with the vacuum pump, *P*, by an air channel, the inlet of which crosses all slit exits.

Each slit channel represents a vertical wedge (7.5°) of rectangular cross section with polished interior surfaces. This configuration was developed to assure uniform acceleration of the airflow up to the exit speed at the slit aperture and to avoid particle deposition by premature impaction within the channels. It also effects maximal flow rates for given pressure differences.

The outlet, *M*, is connected with pump *P* and bypass *O*, so that valve *N* controls the required pressure reduction in *A*, indicated by gage *R* within ±2 torr.

The location of the slit exists relative to outflow into *P* effects a sharp upward reversal of the flow around a knife-edge barrier immediately after its impaction on the slide. This contributes a centrifugal component to the inertial forces of the particles, which increases precipitation efficiency and requires smaller pressure differentials. The slide motion follows the lateral flow direction caused by this asymmetric reversal to avoid spreading particles on slide sections which have not yet been impacted.

The steady movement of B during impaction is produced by revolutions of the micrometer spindle, G, over the distance of 1 inch. G is mounted vacuum-tight into one wall of A, and is driven by the synchronous motor unit, H, over the variable gear transmission, K, which provides a sequence of 10 consecutively increasing speed ratios. As each stage reduces the preceding ratio by a factor of 2, an exponential sequence of slide velocities results, ranging from 2^1 to $2^{10} \backsim$ 1 to 512, when the transmission index of K is varied between $1 \leq \tau \leq 10$.

Another component of the driving mechanism is the automatic switch unit, L, which cuts the power supply after each fourth revolution and thereby produces a defined deposit length of 0.1 inch. This facilitates the production of exactly equal areas with varying deposit densities.

After the slide has moved over the distance available for impaction (1 inch), the power supplies of motor and pump are cut automatically, and the drive is reversed to return B to its starting position. The latter is adjusted to coincide with the zero mark on the micrometer scale of G in order to define the exact limits of each deposit step on the slide, and to relocate them subsequently on the microscope stage for evaluation. For plateau operation, L is bypassed, so that G is driven at constant speed determined by τ over the entire slide length to form a continuous deposit strip.

Theoretical Considerations

As the general theory of particle precipitation by aerodynamic impaction has been developed by numerous authors, only a few aspects are discussed here.

The impaction efficiency for small particles depends on their mass, represented by their kinetic size, d, the velocity, $\bar{v}$, of the flow at the slit exit, and its distance, δ, from the impinged surface. These parameters are defined as follows:

For the rate of inflow, F, into the impactor, the width, w, and length, L, of the slit, the mean impact velocity, corrected for expansion at the slit exit, results as:

$$\bar{v} = \frac{F \times p_o}{w \times L(p_o - \Delta p)} \tag{1}$$

where p_o is the ambient and Δp the pressure difference (indicated by R in Figure 2). Hence, to maintain the same $\bar{v}$ at higher altitudes, Δp must be adjusted to $\Delta p / p_o$ = constant.

For precipitation of atmospheric aerosols, a slit width of $w = 0.15$ mm. and a length of either $L = 4$ mm. for the twin-slit or $L = 2$ mm. for the quadruple-slit unit, proved most effective. At $\Delta p = 90$ torr, $p_o = 750$ torr, the corresponding flow rates are $F = 4$ and 2 liters per minute $\pm 5\%$ for each slit, equivalent to $\bar{v} = 1.27 \times 10^4$ cm. per second = Mach 0.38, when the distance δ between the slide surface and the slit exits is somewhat less than w—i.e., when δ begins to impose a noticeable restriction on F. For most purposes, $\delta = 0.1$ mm. $= 0.67\ w$ produces the most efficient precipitation at the smallest pressure difference.

The impaction efficiency to be expected for the slit dimensions and operating conditions can be defined from Stokes' law as a dimensionless "inertial parameter" (Davies and Ashmond, 1951; Ranz and Wong, 1952), defined by

$$\psi = \frac{\rho \times \bar{v} \times d^2}{18\eta \times w} \times C = A \times d(d + 1.6 \times 10^{-5}) \tag{2a}$$

for the particle diameter, d, its density, ρ, and the gas viscosity, η. C presents the Knudsen-Cunningham factor (Orr and Dallavalle, 1959; Wasser, 1933) which varies with d and the nature of the particle surface, and may be approximated by (Millikan, 1923; Stern *et al.*, 1962)

$$C \times d^2 = 1 + \frac{1.6 \times 10^{-5}}{d} = d(d + 1.6 \times 10^{-5}) \tag{2b}$$

Substituting $\rho = 1$, $\eta = 1.8 \times 10^{-4}$ poise, $w = 1.5 \times 10^{-2}$ cm., and $\bar{v} = 1.27 \times 10^4$ cm. per second in Equation 2a produces

$$\psi = 2.6 \times 10^8 \times d(d + 1.6 \times 10^{-5}) \tag{2c}$$

This parameter, generally termed $\psi^{1/2}$, varies for the size range 0.1 micron $\leq d \leq$ 0.9 micron between $2 \times 10^{-1} \leq \psi^{1/2} \leq 1.6$, which indicates an impaction efficiency for the slit distance used of about 80% for $d = 0.2$ micron and close to 100% for $d \geq 0.3$ micron. A further efficiency increase in the smallest size range with larger exit velocities—i.e., $\Delta p >$ 120 torr—has proved unfeasible, since this may interfere with the surface adhesion of the larger ($d \geq 0.6$ micron) particles by causing them to slip along the slide in the direction of the deflected flow and coalesce into larger particles—i.e., artifacts (Richardson, 1960). However, at relatively low $\bar{v}$, efficiency is considerably increased by the centrifugal effect of the flow reversion. The limitation of $\bar{v}$ and Δp is advantageous also for a different reason. Detailed performance studies of the MSI have shown that the impaction efficiency of an air sample in the lower humidity range $\leq 60\%$ is much improved when the latter is raised to $\sim 80\%$ prior to impaction. This indicates that the moisture contact increases ψ, and thus d. The effect appears not to be restricted to hygroscopic particles, and is probably not caused by "condensation," as the time interval $\delta/\bar{v}$ available for adiabatic expansion between slit exit and impacted surface is $\sim 10^{-6}$ second. This efficiency increase by moisture addition disappears at higher $\bar{v}$; hence the optimal range has proved to be $100 < \bar{v} \ll 150$ m per second for a controlled humidity level at 70 to 90%.

Another critical factor regarding avoidance of artifactual deposits concerns the flow velocity profile at the slit exit. Figure 3, *Left*, shows its vertical cross section parallel to the slide motion as a steep maximum in the center, which is represented by the density variation of the deposit on a stationary slide—i.e., by a much higher particle number at the center than at the deposit borders. Depending on test duration and prevailing aerosol density, this will cause coagulation—i.e., apparent larger particle sizes and a smaller number at the deposit center than on its borders. If the slide, however, moves steadily relative to the slit, a uniform density

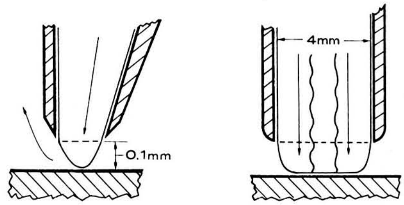

Figure 3. Velocity profiles of air flow between slit exit and slide surface

Left. **Parallel**
Right. **Normal to slide motion**

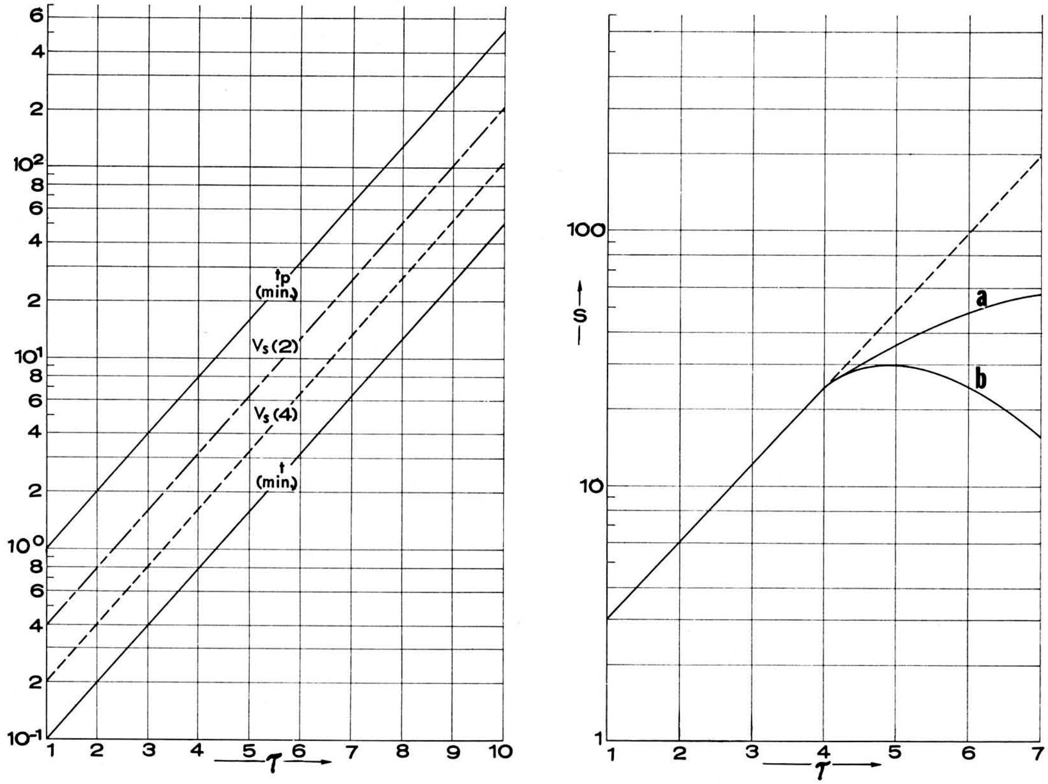

Figure 4. Parameter variation with transmission index

Left. Air volume, V_s, in liters impacted on A_s for twin- and quadruple-slit unit. Time t, t_p in minutes required for each step and plateau formation
Right. Scattering level S *vs.* τ, before ($\tau \leq 4$) and after ($\tau > 4$) critical deposit density. Deviations typify gradual coalescence, *a*, or confluence of droplets, *b*

results and coagulation is avoided if this motion is above the "critical" velocity, beyond which the density must be inversely proportional to the slide velocity.

Figure 3 *Right* indicates the analogous flow profile parallel to the slide—i.e., a uniform lateral density normal to the slide motion.

Evaluation of Impaction Deposits

The air volume represented by one step deposit is

$$V_s = F \times t = F \times \nu \times 2^\tau, \text{ where } \nu = t/2^\tau \qquad (3)$$

ν is determined by the interval t required for formation of one step with a particular transmission index, τ. For the twin-slit unit these parameters amount (within 3%) to: $\nu = 3$, $F = 67$ cc. per second for $\Delta p = 90$ torr, and $A_s = 4 \times 2.5$ mm. $= 10^{-1}$ sq. cm. Hence Equation 3 results in

$$V_s = 2.0 \times 10^2 \times 2^\tau \qquad (3a)$$

V_s can be varied between 0.4 liter for $\tau = 1$ and 205 liters for $\tau = 10$.

The lesser slit lengths of the quadruple slit unit reduce F, A_s, and V_s to one half; hence the deposit density $\sim V_s/A_s$ remains the same. The plateau operation involves 10 step lengths, and the time interval $t_p = 10\ t$ recorded by it can be selected between 1 minute and 8.5 hours. Figure 4 *Left* correlates in a semilog nomogram the values of t, t_p, and V_s for the twin- and quadruple-slit systems, with τ as straight lines of identical slope ($\sim \log 2$).

The micro-optical evaluation of the deposits, by counting either C or light-scattering levels S, must refer to V_f, represented by the fraction A_f of A_s which is measured by the photosensor. From Equation 3a and $A_f = 8$ sq. cm. for 35-mm. film Equation 3b follows

$$V_f(\text{cc}) = \frac{A_f \times V}{A_s \times M} = \frac{80 \times V_s}{M^2} = \frac{2.4 \times 10^2 \times 2^\tau}{M^2} \qquad (3b)$$

Since C and S are proportional to V_f, their variation with τ must follow the same slope (Figure 4) up to a critical deposit density, where coalescence begins which reduces the slope and causes a deviation from the straight line for larger τ. This critical value of V_f facilitates a simple and rapid assay of the prevailing aerosol levels, which does not depend on the optical properties (albedo) of the particulate matter—contrary to evaluations based on light-scattering levels of airborne particles.

The basic requirement for the micro-optical system used for evaluating the slide deposits concerns the traceability of individual particles down to $d \leq 0.2$ micron, regardless of their liquid or solid nature. This condition excludes the use of translucent illumination for two reasons: First, because of the limited optical resolution, since homogeneous immersion techniques cannot be applied without interfering with the constitution of such aerosol deposits; second, because the intense irradiation which must be absorbed by the individual units to render them visible may seriously affect unstable particles after even brief exposure.

By far the most adequate approach to this problem is the application of dark-field illumination, reflected at low angle by highly polished mirror surfaces, upon which the particles are deposited—as originally applied by the author to render the centrifugal deposits of the aerosol spectrometer accessible to counting and microphotometry (Goetz and Kallai, 1964; Goetz and Preining, 1960).

The surface of S is focused by the objective, O. Its aperture ($a = \sin \alpha$) can receive only light scattered within the angle α. The illuminating system provides a converging light beam at an angle β relative to S, which encircles the full azimuth (360°) and is independently adjusted to be confocal with O. Figure 5 shows the optical scheme. As the surface of S represents an opaque, nonscattering mirror, the optical field is completely dark, provided β is sufficiently low, so that the reflected light cannot enter the aperture a, i.e. $\beta < (90° - a)$. If, however, particles are deposited on S, a fraction of the light scattered by each unit enters the objective, and an image of each light-scattering center is formed. These images, however, do not present the true particle sizes, if they are below the resolving limit.

Objectives of relatively small numerical aperture ($a \leq 0.6$), and relatively low magnification ($M \leq 25X$) are used to form the microscopic image. As most of the light is reflected by the slide surface and scattered by the particles, thermal effects and potential degeneration are minimized.

A micro-optical unit which meets these requirements well is the Ultrapak-system with ring-condenser (Leitz-Wetzlar), as the latter can be adjusted independently from the objective focus to effect optimal dark field for the mirror slides. The microscope unit (Zeiss) (Figure 6), specifically assembled for slide evaluation, accommodates visual binocular observation as well as photographic and photometric evaluation. For the latter, the optical beam is shifted either to a 35-mm. film camera or to a photocell with amplifier, which indicates the S-value of A_f. For identification of the individual slide deposits, the scales of the cross stage are marked to coincide with the centers of each τ step on the two- or four-deposit strips. The design of the substage facilitates shifting the slide sideways sufficiently far from the objective to expose the deposits to a variety of conditions (ultraviolet, thermal, or moisture) without removing the slide from the stage. Thereby exact relocation of the optical field for subsequent observation is possible.

Photometric evaluation differs in principle from customary methods for determining aerosol densities from the light-scattering intensity of airborne particles within a limited (three-dimensional) air volume, defined by the illuminating light beam. The method of evaluating the scattering capacity of a two-dimensional area (A_f) upon which the particles of a defined air volume (V_f) have been precipitated is new and much more sensitive. Since the density of the precipitate can be varied more than 500-fold, the lower sensor limit is larger by several orders of magnitude for the same photometer sensitivity than that of the three-dimensional evaluation—provided that all particle sizes which are significant scattering contributors are precipitated.

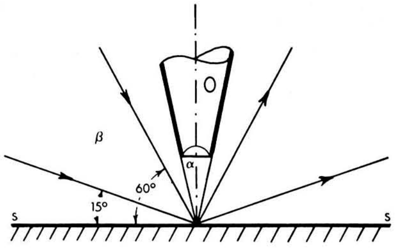

Figure 5. Scheme of micro-optical system for slide evaluation

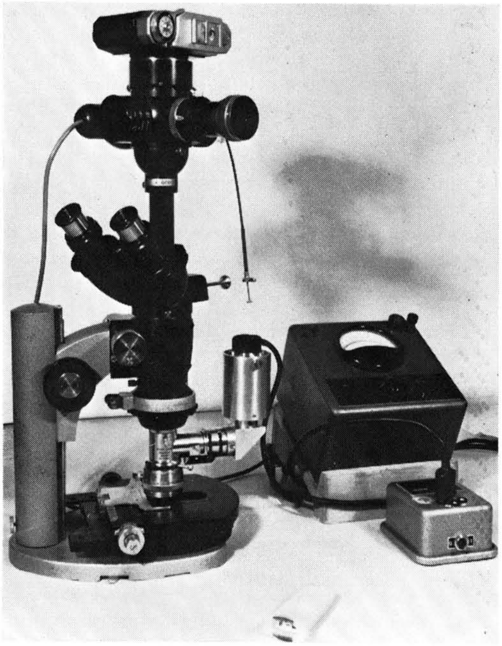

Figure 6. Microscope assembly for optical, photographic, and microphotometric slide evaluation

Another advantage, important for many applications, is the preservation of the particles for evaluating their stability by the variation of the S levels after exposing the slides to various destructive conditions, such as vacuum desiccation, heat, ozone, and ultraviolet irradiation.

Obviously, the sensitivity of this method is limited by the scattering level, S_o, of the clean slide surface, as it represents the background above which a particle can be seen. Hence, S_o determines the lower threshold of identifiable sizes under reflected dark-field illumination, in analogy to the micro-optical resolving power limit with translucent illumination.

Extended efforts have proved the feasibility of producing metallic surfaces of very low scattering levels which fulfill the condition of the smallest particle size limit. The most successful type so far is a glass microslide, upon which an opaque chrome-nickel layer with a protective thin coating of SiO is evaporated in high vacuum.

Another significant factor which determines impaction efficiency, especially in the smallest size range, is the adhesive retention of the particles, which depends on their affinity with the chemical constitution of the slide surface. Extended tests with atmospheric aerocolloids have shown that a hydrophobic monolayer produces deposits suitable for microscopic evaluation of the smallest particle sizes, as it prevents their premature coagulation. This surface layer is produced by brief exposure (≤ 1 minute) of the cleaned slide to the vapor of monochlorotrimethylsilane, followed by contact with gaseous ammonia for neutralizing the HCl traces resulting from the surface reaction of the silane. The slides can be used many

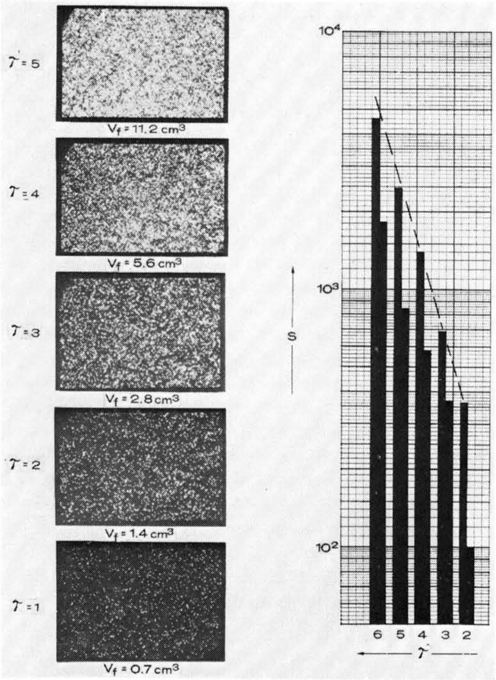

Figure 7. Microphotographs

Left. **Deposits from monodisperse latex aerosol for five deposit densities (1 to 16)**
Right. **Corresponding** *S* **levels before and after ultraviolet irradiation**
– – – Predicted slope (~ log 2)

times, if the deposits are removed by liquid contact with detergents or solvents which remove the surface layer bearing the particles. This silane treatment must be applied within a few hours before impaction.

The micro-optical evaluation of the deposits is not restricted to metallic surfaces, when larger sizes are involved. Transparent slides can facilitate, for example, colorimetric evaluation by transmitted light.

Instrument Performance

Figure 7 *Left* shows a series of microphotographs obtained from a dry air flow into which an aqueous suspension of monodisperse latex particles (d = 0.26 micron) was nebulized. The deposits were produced on metallic surface slides and photographed by the system described above. Figure 7 *Right* shows the corresponding diagram of S levels for the five τ steps, prior to and after extended exposure to ultraviolet irradiation, where partial photochemical oxidation of the polysterene particles is indicated by reduction of S.

For environmental air sampling, the mode by which the air is brought to the MSI must avoid aerocolloids inevitably dispersed by the personnel and operation of the equipment. Figure 8 schematically shows the setup developed for this purpose: A is the flexible plastic tube (2-inch i.d.) of suitable length (30 to 60 feet) through which a continuous flow is produced by a small blower, B, whereby the residence of the air within A is reduced to a few seconds. C is a flexible metal tube (0.75-inch i.d.) mounted concentrically within A to neutralize the suction by B in the flow fraction led to the MSI. This fraction is then split into two branches which pass through geometrically identical channels D and W. While the passage through D does not alter the ambient conditions, W increases the humidity of the flow by its water-impregnated wall linings to 75 to 80%. In the same manner, additional branches can be provided in which the flow is briefly exposed to ultraviolet irradiation, which can markedly alter the aerocolloid levels (Goetz, 1968).

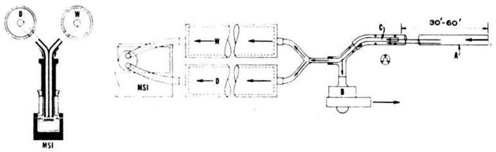

Figure 8. Induction system for atmospheric samples

- *A.* **Plastic hose**
- *B.* **Blower**
- *C.* **Concentric sampling tube**
- *W.* **Humidifying channel**

As an example, Figure 9 shows step patterns taken during a smog period below the inversion layer in the Los Angeles Basin, with and without prehumidification. Figure 10 presents a typical S-level pattern which indicates about a sixfold increase for the prehumidified samples (W). The deposits were subsequently exposed for ~20 hours to intense ultraviolet irradiation, which caused the gradual decay of the particulate matter, as indicated by the S levels in good proportion to the density levels, τ.

Samples of this type have been taken over a wide variety of atmospheric conditions during day and night, including many samples of the air immediately over the ocean, which

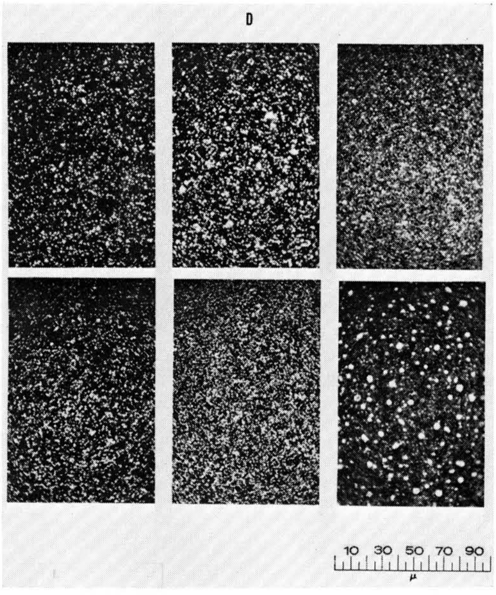

Figure 9. Deposits from urban air mass contained in air volumina

Upper row. **Without prehumidification**
Left. τ = 3. V_f = 2.8 cc.
Center. τ = 4. V_f = 5.6 cc.
Right. τ = 5. V_f = 11.2 cc.
Lower row. **With prehumidification**
Δp = 60 torr

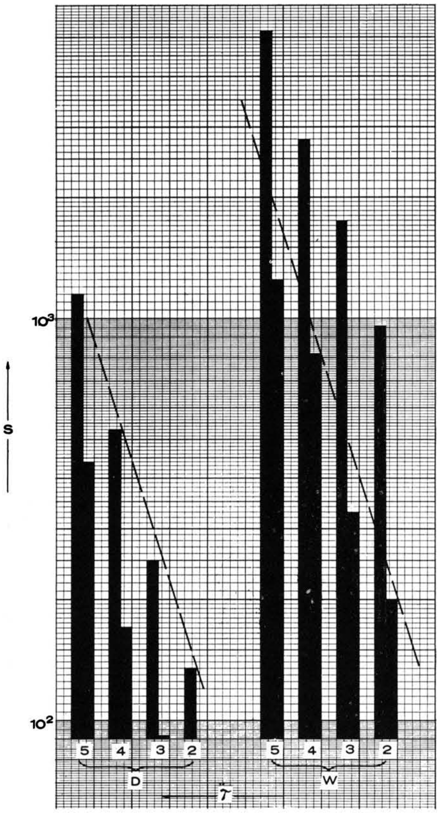

Figure 10. *S*-level pattern of deposits in Figure 9 after passage through *D* and *W* channels

Left. **Prior to exposure**
Right. **After extended (6-hour) ultraviolet exposure**

showed to a major or minor degree the thermal and photochemical instability of the aerocolloidal matter prevailing in hazes and smogs (Goetz, 1960; Goetz and Preining, 1961; Goetz *et al.*, 1961).

Comparison of simultaneous multiple-slit deposits showed particularly remarkable alterations if branches of the flow were briefly (6 to 30 seconds) exposed to ultraviolet ($\geq$1800-A) irradiation prior to impaction. In this manner it has been possible to observe lasting particle formation by atmospheric traces of gaseous reactive hydrocarbons, due to oxypolymerization induced by the irradiation exposure.

Acknowledgment

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Application of the instrument to atmospheric studies has been continued and certain instrumental improvements effected since, at the laboratories of Atmospheric Research Group—Altadena with U. S. Public Health Service support (Grant AP00543-01/03).

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Under license from the California Institute Research Foundation, Meteorology Research, Inc., now produces a commercial model of the MSI.

Nomenclature

A_s = area of one deposit step, mm.
A_f = area exposed to photosensor
d = Stokesian particle diameter
F = flow rate at slit inlet, liters/min.
L = length of slit exit, mm.
M = linear magnification of micro-optics
p_0 = ambient air pressure, torr
Δp = pressure difference across slit, torr
t = time interval for one step deposit
$\bar{v}$ = mean flow and impact velocity at slit exit, cm./sec.
V_s, V_f = air volume impacted on A_s, A_f,
w = width of slit exit, mm.

GREEK LETTERS

δ = distance of slit exit from impinged surface, mm.
η = viscosity
ν = index ratio
ρ = particle density
τ = transmission index
ψ = intertial parameter

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Application of Internal Reflectance Spectroscopy to Water Pollution Analyses

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■ Colorimetric and spectrophotometric analytical methods are useful in both qualitative and quantitative analyses in aqueous systems, but a serious drawback in such conventional transmission methods is that the sample must be a homogeneous, transparent solution. The use of internal reflectance spectroscopy, however, circumvents separation steps which must be employed with optically opaque samples. With this technique, direct spectrophotometric analyses of marine sediments, water filtrates, aqueous suspensions, etc., can be carried out. Both visible colorimetric and infrared spectrophotometric methods are described in this paper, along with some representative data and the experimental apparatus, pointing out the potentialities of this technique.

Attentuated total reflectance, the principle of internal reflectance spectroscopy, has long been used in the measurement of refractive index (Simmons, 1959). Later, the application of attenuated total reflectance spectroscopy (ATR) as a method for obtaining infrared spectra of opaque materials was introduced (Fahrenfort, 1961; Harrick, 1960). Cell designs and methods for obtaining multiple internal reflection spectra in the UV, visible, and near-infrared regions were developed by several groups (Hansen and Horton, 1964; Harrick, 1967.)

In internal reflection spectroscopy (IRS), monochromatic light is injected into a crystal of suitable refractive index, n_1, which in turn is in contact with the sample medium, refractive index = n_2 (Figure 1). If the crystal surface is highly polished, and the angle θ is greater than the critical angle θ_c (defined by $\theta_c = \sin^{-1} n_2/n_1$), total internal reflection will take place at the interface. As shown in Figure 1, the x-components of the incident and reflected waves combine to form a standing wave on the crystal side of the interface. An evanescent wave is also produced, which penetrates into the sample medium; the amplitude of the evanescent wave decays exponentially with increasing distance into the sample. The range of penetration is on the order of $\lambda/7$ to $\lambda/10$.

The presence of a photo-active species on the sample side of the interface will cause absorption of energy from the evanescent wave, and transfer of energy across the interface. This loss of energy to the absorbing species in the sample is seen as an attenuation of the reflected beam.

By increasing the number of reflections at the crystal-sample interface, the resulting attenuation is increased proportionally. Figure 2 shows a multiple internal reflection cell for visible light. The laser beam is shown entering the glass plate through a refracting prism, then making nine reflections between the prisms before exiting from the other refracting prism.

The attenuation of the light passing through an IRS cell is monitored and recorded just as in the case of a transmission spectrum. There is no shift in frequency between the light in the crystal and the evanescent wave, but the resulting internal reflection spectrum shows absorptions at slightly shifted wavelengths from a transmission spectrum. These shifts are generally small—i.e., 2 to 15 cm.$^{-1}$—and can usually be ignored. The reflectance is, however, a function of both changes in κ, the optical absorption coefficient, and η, the measured part of the refractive index, with wavelength. These are related by

$$n(\lambda) = \kappa\eta(\lambda) + i(\lambda) \tag{1}$$

where n is the complex refractive index. Because of the influence of the refractive index on the observed attenuation, the internal reflection peaks do not show the same intensity relationships as the peaks in a conventional transmission spectrum.

Experimental

Infrared Studies. Qualitative and semiquantitative infrared internal reflection spectra were obtained with a Wilks Scientific Model 12 multiple internal reflection accessory, used with a Perkin-Elmer Model 337 grating spectrophotometer. The Wilks MIR-12 consists of four adjustable mirrors and a

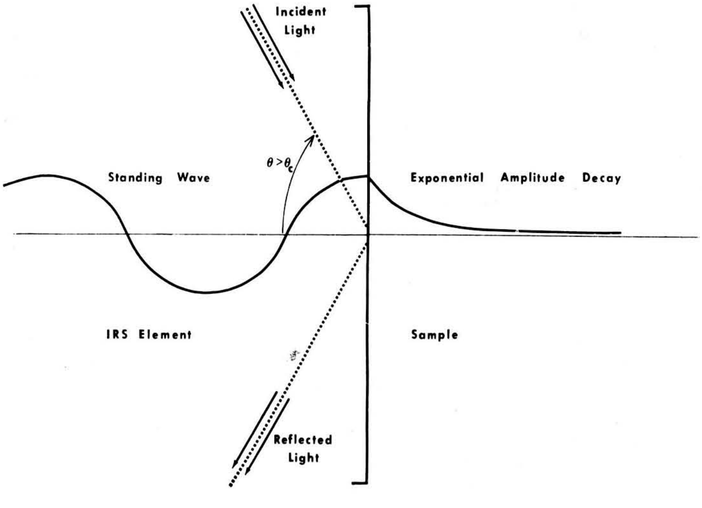

Figure 1. (attenuated) Total internal reflection

Energy is transferred to an absorbing sample via the evanescent wave,

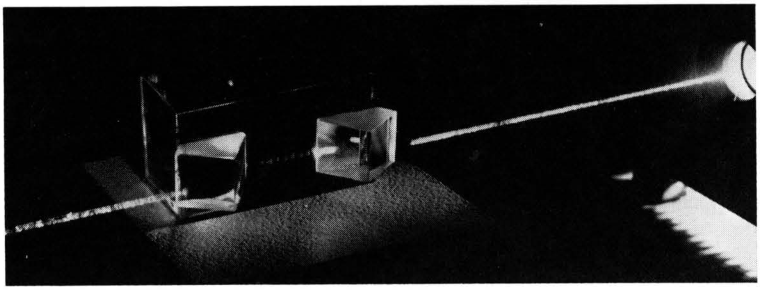

Figure 2. Multiple total internal reflection

Shown is the light from a gas laser entering a multiple reflection cell via a refracting prism, making nine reflections as it passes down the 1-mm.-thick glass plate, then exiting via a similar refracting prism (Photograph by Paul Earl, U.S. Bureau of Commercial Fisheries, Ann Arbor, Mich.)

sample-crystal holder for each beam of the instrument. With the mirrors adjusted for maximum output from the crystal in the sample beam, intensities of 60% for KRS-5, 40% for silver bromide or silver chloride, and 15 to 20% for germanium (relative to the amount of light passing through an empty sample compartment) can be obtained. These large amounts of available light coming through the crystals enable the photometer section of the instrument to operate as well with the internal reflection accessories in place as it does in the transmission mode. In addition, an *x-y* recorder was connected, for certain experiments, to the scale expander of the Perkin-Elmer 337, which gave an increase in sensitivity of at least one order of magnitude.

In the spectral study of solid particulate matter obtainable as filtrates, the material was collected on a Millipore filter using a previously described technique (Hannah and Dwyer, 1964). Figure 3 shows the sandwich arrangement used to obtain optical contact between the sample material on the filter and the IRS crystal. Pieces of rubber dental dam were interposed between the sample filters and the glass plates to take up the pressure of the tightening screws and avoid breaking the brittle IRS plates. The filters themselves give a complicated infrared spectrum if allowed to come into optical contact with the IRS crystal. To avoid this, it is necessary to have the coating of the sample material on the filter sufficiently thick to ensure that only the sample spectrum will be obtained. Because of the limited penetration depth of the evanescent wave, a uniform coating of 3 mg. of material over 10 cm.^{2} on a filter surface provides sufficient protection against observing bands of the filter itself.

The use of reference beam subtraction of the substrate spectrum is discussed in a paper on the spectra of active carbons (Mattson, Mark, *et al.*, 1968), and this technique can be applied generally in IRS analyses.

Water samples require another handling procedure. They were injected into a Wilks liquid sampling cell, which requires about a 2-ml. volume of sample. In this case, germanium provides the best IRS crystal material because of solubility problems with other materials, even though it does not transmit beyond 11 microns. However, the germanium range is sufficient to accomplish organic identification in aqueous samples within the water "windows," which are from 3 to 6 and 6.5 to 11 microns. The former water window allows group frequency bands to be measured, and the latter is in the fingerprint region. KRS-5, a material which transmits further out into the infrared and passes the most IRS light through it, is unsatisfactory for aqueous samples. This material, a mixture of thallium bromide and thallium iodide, is slightly soluble in hot water. When infrared light hits the KRS-5/water interface, it heats up the water sufficiently to destroy the reflecting ability of the crystal surface. Silver halide crystals transmit further into the infrared and pass more IRS light than germanium, but they have proved unsatisfactory because of their tendency to corrode the stainless steel sample cells used in this study. The oxides collecting on the crystal eventually damage the reflecting surface. It is possible that Teflon or other plastic materials can be used as cell materials, which would circumvent the problem. At present, work is under way in this area.

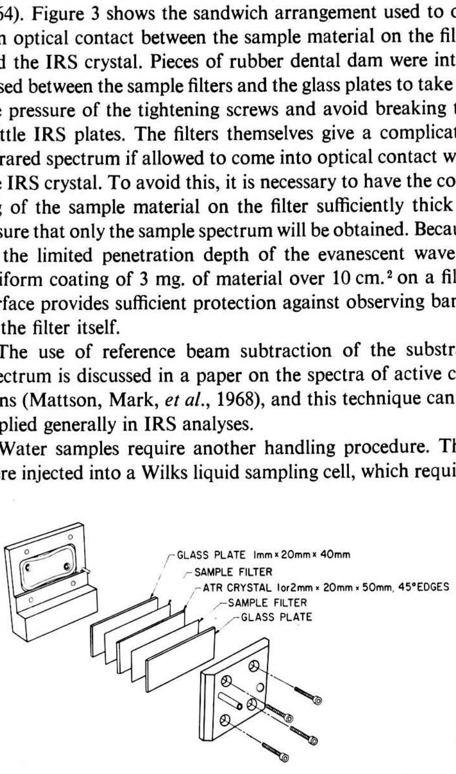

Figure 3. Sandwich arrangement

This arrangement was used to obtain infrared spectra of particulate matter entrapped on microporous filters. The glass plates are used to obtain uniform optical contact between the ATR crystal and the sample filter

Still other samples require handling in another way. Sediment samples can be placed in the cavities of the Wilks liquid cell, the crystal included, and the cell assembled with the sample in place. This method is favored for a large range of samples, both wet and dry particulate matter, where the amount of sample available is not a limiting factor.

Visible Region. For the region from 3500 to 8000 A., a Cary Model 14 spectrophotometer was used. The cell pictured in Figure 2 was used, and an optical cement with a refractive index matching that of the glass was employed to hold the prisms in place (Lens Bond M-60, Summers Laboratories, Fort Washington, Pa.). Several cells of this general type were used, some with the refracting prisms shown, others with an achromatic arrangement employing reflecting prisms. For this type of work, the achromatic arrangement is favored.

Substitution of fused quartz for the reflecting plate and the prisms provides access to the UV and near-IR regions with the same experimental setup.

Applications

Infrared IRS. Figures 4 and 5 show spectra obtained with the microporous filter sandwich. In Figure 4, three cigarettes were "smoked" by an aspirator with the smoke passing through a 0.45-micron filter, and the spectrum of the entrapped solids was taken.

Figure 5 shows the comparison of the infrared spectra of two different species of blue-green algae. These organisms were cultured by the U.S. Bureau of Commercial Fisheries and filtered onto 0.45-micron filters for analysis. The technique

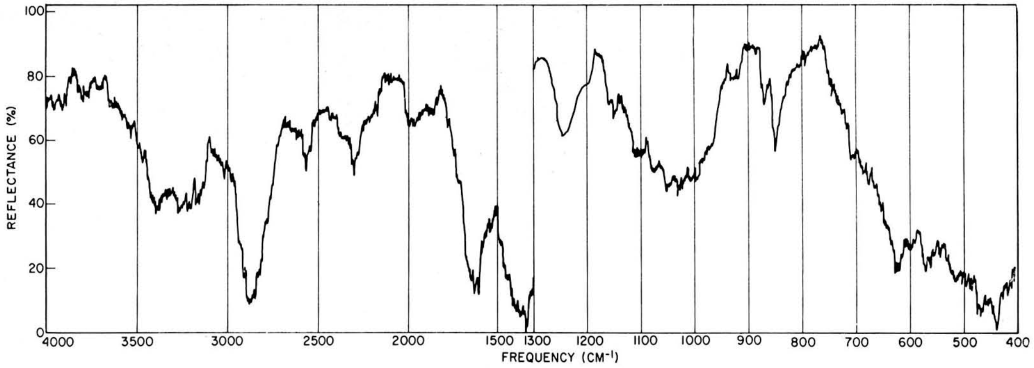

Figure 4. Cigarette smoke

Infrared internal reflectance spectrum of solid material filtered from smoke of three Camel cigarettes. Identification of some of the observed bands includes: 3400 to 3200 cm.$^{-1}$–OH, 2900 cm.$^{-1}$–C—H, 2300 cm.$^{-1}$–C—N, 1650 cm.$^{-1}$–C—O, 1350 cm.$^{-1}$C=H. IRS crystal was KRS-5

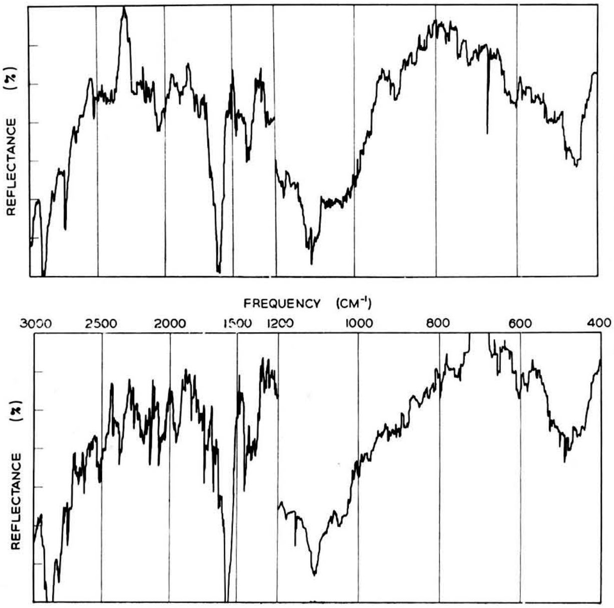

Figure 5. Blue-green algae

Infrared internal reflection spectra (about 5× scale expansion) of *Anabaena cylindrinca* (top) and *Naviola pellicolosa* (bottom). Identification of major peaks includes: 2900 cm.$^{-1}$–C—H, 1600 cm.$^{-1}$–C=O, 1400 cm.$^{-1}$–C—H. IRS crystal was KRS-5

opens new paths to the study of the chemical nature of microorganisms. The two species exhibit characteristic spectra, with definite differences which may be correlated to organic compounds making up the structure of the organisms. It may be possible to resolve the spectra of mixed cultures occurring naturally by the use of a computer. The computer would determine which types of organisms were present by comparison of peak areas and locations, with reference spectra of pure strains stored in a computer memory file.

Figure 6 is the spectrum of Lake Erie bottom mud, showing the presence of carbonyl groups at 1750 cm.$^{-1}$, as well as the expected water peaks at 3 and 6 microns (only the group frequency range is shown in this figure). In spectra of bottom sediments, it is possible to use germanium IRS elements and obtain information on carbonyl, nitrile, ether, and other organic functional groups which exhibit characteristic vibrational frequencies in the 2- to 11-micron region. The method offers many advantages over previous identification methods

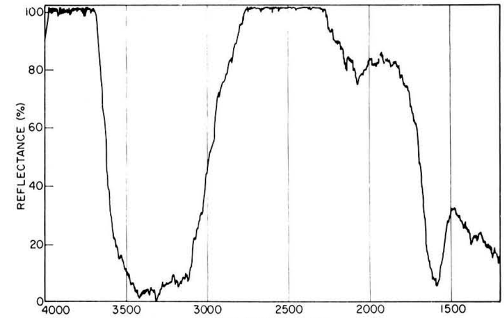

Figure 6. Lake Erie sediment

Infrared internal reflection spectrum taken directly on sample with no drying or other preparation. Major peaks observed are those of water. IRS crystal was Ge

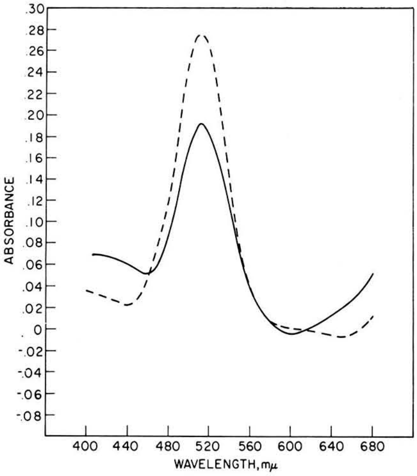

Figure 7. Eosin-B: Reflectance vs. transmittance

The solid line is a reflectance spectrum of a solution of Eosin-B obtained (with the cell in Figure 2) in a Cary Model 14 spectrophotometer. The broken line is a transmission spectrum obtained in the same instrument. With nine reflections, and small absorbances, the maxima occur at nearly the same wavelength

for these materials. There is no need to separate water from the samples, nor is there any separation step necessary. It is not necessary to filter or digest any of the solid material in the sample. Because the sample is analyzed directly and wholly intact without any pretreatment, there can be no losses, degradation, or change of components from separation and concentration steps. The method is seen to be readily adaptable to shipboard and field use.

Visible IRS. Conventional colorimetric methods require a homogeneous, transparent liquid for accurate and reliable determinations. With a total internal reflection optical path, the light beam never enters the sample and thus is not susceptible to scattering. For this reason, colorimetric determinations may be carried out in mixed or nonhomogeneous media, especially wet sediment. An example system is described below.

Figure 7 shows the absorption peak of an Eosin-B solution, an intense red dye. As is seen in this figure, the reflection peak occurs in the same wavelength region as the transmission peak.

By mixing Eosin-B with kaolinite and distilled water, a slurry consisting of 70% water and varying concentrations of dye from 0.16 to 16 parts per thousand (p.p.t.), a synthetic sediment system was formed. The reflectance was obtained using the cell in Figure 2, and the plot in Figure 8 shows a good Beer's law relationship at 4900 A. Beyond the range of this plot (dye concentrations greater than 1.6%) the highly intense dye shows a falling off of the linear relationship, as would be expected. Below the level of 0.61 p.p.t., the measured absorbances were too low to be determined using the cell shown in Figure 2. This cell has only five reflections on the sample side of the reflection plate. By decreasing the thickness of this plate from 1.5 mm. to 0.15 mm., an increase of sensitivity of an order of magnitude is obtained by getting 50 reflections on the inner side of the plate. By more judicious optimization of cell design, it is possible to obtain a total of over 400 reflections (Mattson and Mark, 1968), and by placing sample material on both sides of the reflection plate, the sensitivity is extended to the parts-per-million range. Therefore,

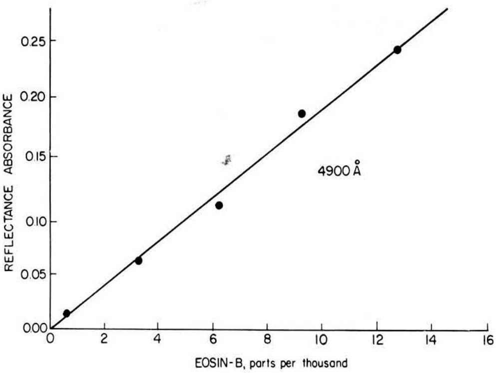

Figure 8. Kaolinite–water–Eosin-B slurry

In a mixture of about 70% kaolinite, it is still possible to obtain a reasonable Beer's Law plot for the species in solution, using visible attenuated total internal reflection

quantitative determinations may be made using coupled color forming reactions carried out in the sediment itself (Mattson and Mark, 1968) in mud from a level of a few parts per million up to a few per cent, with a colored species with a molar extinction coefficient around 10^4.

Kaolinite has a particle size in the colloidal range, so that a slurry of it does not show any settling or phase separation during the time needed for analysis. However, larger particle sizes, such as occur naturally, have a tendency to settle rapidly. For these, the internal reflection plate must be located at the bottom of the cell, rather than the side, for reproducible results.

Conclusions

It is possible for direct optical chemical analyses to be carried out in previously unusable sample media, and to identify organic components of optically opaque materials by the technique of total internal reflection spectroscopy. This is important to the analyst of the environment, as a tool which can cut hours off analysis time spent in separation, digestion, filtration, etc. It provides a reproducible spectrum of a completely opaque material which can be used for further study of natural systems.

Acknowledgment

We acknowledge the assistance of Herbert E. Allen and Paul Earl of the U. S. Bureau of Commerical Fisheries, Ann Arbor, and thank Paul Wilks, of Wilks Scientific Corp., for donation of the MIR-12 which made this work possible.

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Application of Semipermeable Ion Exchange Membranes to *In Situ* Determination of Trace Metal Ions in Aqueous Systems by Electrochemical and Neutron Activation Techniques

Critical Evaluation of Techniques

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■ Ion exchange membranes are employed in conjunction with neutron activation analysis and anodic stripping voltammetry to determine certain trace metal ions in aqueous media. As these two analytical techniques or applications with ion exchange membranes appear on the surface to have considerable promise with respect to *in situ* analysis in natural water systems, the parameters which govern their applicability, limitations, and sensitivity were investigated. This study showed these techniques to be somewhat impractical for routine trace analysis. The relationships (or proportionality factors) relating the measured amounts of material and the concentrations of these species in their original environment are complex, although they can be treated quantitatively. Furthermore, very long times are required for trace systems to reach equilibrium. In both analytical techniques, the ion exchange membrane is used as an *in situ* preconcentration matrix prior to actual analysis. Experiments were carried out to determine if large surface active organic materials in natural systems inhibit exchange by passivating or blocking the surface, which would make the analysis of nature systems impossible by this technique.

If a cation exchange membrane is allowed to equilibrate in an aqueous medium containing one or more metal ions, the membrane will show an increased concentration of metal ions with respect to the original concentration in the aqueous system (Helfferich, 1962). It was originally suggested, therefore, that such membranes could be employed for a simple *in situ* metal ion analysis technique (Berlandi, 1966). Small disks of an ion exchange membrane could be equilibrated in the natural water system, such as a lake, ocean, or sewage system, then returned to the laboratory to determine the metal ion(s) concentration in them, using either neutron activation analysis of the membrane directly or an anodic stripping technique in which the pre-equilibrated membrane is mounted near the electrode during the electrodeposition step of stripping voltammetry (Eisner, Rottschafer, *et al.*, 1967). If the equilibrium constants of the ion exchange membrane in the system under analysis are known, the initial concentrations of the metal ions can be calculated from the concentrations of these species in the membrane. Parameters, such as equilibration time, distribution coefficients, and effects of electrolyte concentrations, which govern the applicability, limitations, and sensitivity of this technique are discussed.

Experimental

Reagents and Apparatus. All reagents were analytical grade, used with no further purification. Deionized water, which was then double-distilled (with potassium permanganate in the first stage of distillation) was used for preparing all stock solutions and for further dilutions.

Prior to use, the ion exchange membranes were washed in $1M$ KOH to remove oil and surface contaminants and then in $1M$ HNO_3 and double-distilled water. The washed membranes were stored in water until needed.

Stock solutions, prepared by standard methods, of $0.1M$ concentration were made for each of the ions—silver, copper, cobalt, and indium—used in this study. Working solutions were then prepared daily by dilution of the stock solutions.

The zinc tracer solutions were prepared by irradiating 2 mg. of zinc metal (encapsulated in quartz for 24 hours in the reactor). The irradiated metal was then dissolved in nitric acid and the solution diluted up to 10 ml. The activity of the final solution ($3.28 \times 10^{-3}M$ Zn^{+2}) was about 30,000 counts per minute per ml. of solution.

The construction as shown in Figure 1 and operation of the membrane "barrier" electrode assembly have been described (Eisner, Rottschafer, *et al.*, 1967).

The electrodeposition and anodic stripping voltammetry were carried out in a three-electrode cell, using instrumentation constructed from the basic operational amplifier circuits of DeFord (DeFord, 1958; Vassos, 1965) and were recorded by a Moseley Autograph model 2D-2M X-Y recorder. The scan rates used throughout this study were 5 to 30 mv. per second.

All activation irradiations were carried out in the Ford Nuclear Reactor of the Michigan Memorial Phoenix Project,

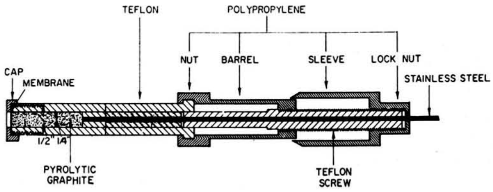

Figure 1. Electrode assembly

which has a thermal neutron flux (in the pneumatic tubes) of 5×10^{12} neutrons per sq. cm. per second. The gamma counting and spectroscopy of the irradiated samples were accomplished with a RIDL 400 channel analyzer using a 3×3 NaI (Tl) scintillation crystal.

Preconcentration of Metal Ion in Membrane. The cation exchange membranes (C103, American Machine and Foundry Co., Springdale, Conn.) were equilibrated with the solution to be analyzed, using a constant stirring rate (Vassos, 1965), then removed and rinsed with water. The trace metal ion was determined by neutron activation analysis or by anodic stripping voltammetry.

Neutron Activation Analysis. The pre-equilibrated membranes to be analyzed by neutron activation analysis were encapsulated in a polyethylene vial. The size of the membrane disks (10-mm. diameter) matched the inside diameter of the vial, so that they had no free movements within it. The pneumatic polyethylene rabbit was also milled, so that this vial fitted exactly without free movement. Thus, a constant geometry for irradiation was maintained through the experiments, keeping the neutron flux in the membrane as constant as possible (Berlandi, 1966).

After irradiation, the membrane was removed from the vial, enclosed in a new vial, and placed in the counting chamber. Removing and re-encapsulating took less than a minute, enabling the use of isotopes with half lives as short as 30 seconds in these determinations.

Anodic Stripping Voltammetry. For the anodic stripping voltammetry determinations, the membranes were also pre-equilibrated and rinsed as described above. The membrane electrode was assembled (Figure 1) and electrolysis carried out using a solution of the supporting electrolyte alone. (Eisner, Rottschafer, *et al.*, 1967, discuss mechanics of this operation). As the only ions available for deposition on the electrode are those initially attached in the membranes, stirring has no measurable effect on the deposition step and the electrolyses were, thus, carried out in a quiescent solution. The dissolution step was carried out in the same solution after removal of the membrane (Eisner, Rottschafer, *et al.*, 1967).

Results and Discussion

Ag^+, Cu^{+2}, Zn^{+2}, Co^{+2}, and In^{+3} were employed in various combinations to demonstrate the applicability of the methods described. As these ions are easily determined by radioactivation analysis techniques, the parameters to be considered in the exchange processes involved were investigated by this method.

Equilibration Time of Membrane. The membranes were equilibrated in stirred solutions at 25° C. In all experiments, the volume of bulk solution involved in the equilibration was sufficiently large so that the concentration of the ion of interest remains virtually constant in the solution during the equilibration experiments. As the concentration of the counter ion initially in the membrane is high (~1 meq. per gram), the theoretical treatment of the exchange process can be described by the same equations employed for isotopic exchange processes that are governed by film diffusion alone. The rate of exchange is thus proportional to the concentration of the trace ion in the bulk solution diffusing to the membrane (Helfferich, 1962).

Experimentally, the equilibration time for a particular metal ion varied proportionally with concentration of the ion present in the bulk of solution, as expected for a diffusion-controlled process. Thus, it is necessary to know the approximate levels of the concentration of the trace species to know how long to allow the membrane to be in contact with the sample solution. For a $10^{-4}M$ solution the equilibration time is approximately 30 minutes; for a $10^{-5}M$ solution, about 300 minutes; and for a $10^{-6}M$ solution, 30 hours. This, of course, is a disadvantage to the use of this technique in analysis. However, as the rate of attaining equilibrium is essentially linear as a function of time (Figure 2), the ion exchange membrane can be left in contact with the solution for a fixed time interval. If the equilibration rate constant (the proportionality constant relating concentration of ion in the membrane with the initial concentration of the ion in the bulk solution as a function of time) is predetermined, the analysis of the membrane can be used to calculate the initial concentration in solution. Of course, considerable sensitivity is lost, if the system is not allowed to reach equilibrium.

The equilibration rate and equilibration time were also functions of the particular cation being determined (Figure 2). Thus, again it is necessary to know which cations are present and in what concentration level, in order to know how long the membrane must be in contact with the solution to reach equilibrium, or to know the equilibrium rate constants in order to use a fixed time method (with the usual loss of sensitivity). The equilibration times for the trace metal ions were found to be essentially independent of the alkali metal ion concentration of the supporting electrolytes. Thus, the nature of the water system—fresh, brackish, or sea—does not affect the equilibration time.

Determination of Distribution Factor of Metal Ion between Solution and Membrane. The degree of enrichment of the metal ion of interest in the membrane was also found to be related to the ion which undergoes the exchange. The exchange is a dynamic process and the enrichment takes place until the ion in the membrane reaches a certain equilibrium concentration. A useful way to define the extent of enrichment is the distribution factor, D_i:

$$D_i = \frac{\text{mg. metal in membrane} \,/\, \text{g. membrane}}{\text{mg. metal in solution} \,/\, \text{g. solution}}$$

The D_i values arise from several chemical characteristics of the various ions, such as valence, charge density, and size. The experimental values of D_i for the particular ions under investigation (in $0.1M\ KNO_3$) are shown in Table I.

In contrast to the equilibrium time, the D_i values vary with the concentration of the gross components (on supporting base electrolyte) in solution. In the case of ion exchange resins, the value of D_i is inversely proportional to the electrolyte concentration (Samuelson, 1963):

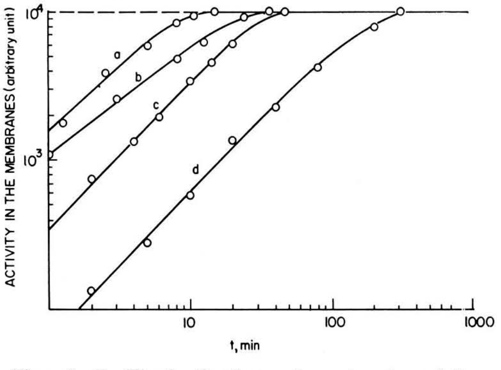

Figure 2. Equilibration time for membranes in various solutions

a. $3 \times 10^{-4}\ M\ Co^{+2}$, $0.1M\ KNO_3$, *b.* $2 \times 10^{-4}M\ Ag^+$, $0.1M\ KNO_3$, *c.* $2 \times 10^{-4}\ M\ Cu^{+2}$, $0.1M\ KNO_3$, *d.* $2 \times 10^{-4}\ Zn^{+2}$, $0.01\ M\ NO_3$

Table I. Distribution Coefficient or Factor, D_i, for Metal Ions in $0.1M$ KNO_3 Solutions

Ion	D_i
Ag^+	30
Co^{+2}	240
Zn^{+2}	250
Cu^{+2}	400
In^{+3}	13,000

$$D_i = \text{const.}\ \frac{1}{A^{i/a}} \tag{1}$$

where A is the concentration of the electrolyte, i is the valence of trace element, and a is the valence of the bulk ion.

A study was made to determine if this relationship was valid also for the ion exchange membranes when KNO_3 was used as the base electrolyte and Ag^+, Co^{+2}, Cu^{+2}, and In^{+3} as the trace elements. While the plots of log D_i *vs.* log A were linear, as expected, the slopes were −0.86, −1.20, −1.15, and −1.25, respectively, for the trace elements (Figure 3), differing considerably from the predicted slopes of −1.0, −2.0, −2.0, and −3.0 (Samuelson, 1963). The reason for this disagreement is not understood at this time; however, certain conditions imposed on the derivation of Equation 1 may not be met in the membrane case (Samuelson, 1963).

Thus, it is necessary to know the distribution factor for each metal ion measured under the same electrolyte concentration as that of the sample bulk solution of interest, in order to calculate the concentration of the trace species in the sample bulk solution from the measured values in the membrane.

Application of Pre-equilibrated Membranes as a Preconcentration Matrix for Neutron Activation Analysis. Analytical calibration curves (activity in the membrane *vs.* bulk concentration, slope equal to D_i) in $0.1M$ KNO_3, for Cu^{+2} and Ag^+, were found to be linear over the 10^{-4} to $10^{-5}M$ concentration range, for In^{+3} over a 10^{-6} to $10^{-7}M$ range, and for Co^{+2} over 1×10^{-4} to $5 \times 10^{-5}M$ range. The factors which determine the sensitivity of utilizing the equilibrated membrane as a preconcentration step for neutron activation analysis are D_i and the usual parameters, such as cross section, isotopic abundance, and half life, that are inherent in activation analysis (Crouthamel, 1960). The various parameters of importance for the ions Ag^+, Co^{+2}, Cu^{+2}, and In^{+3} are summarized in Table II and below.

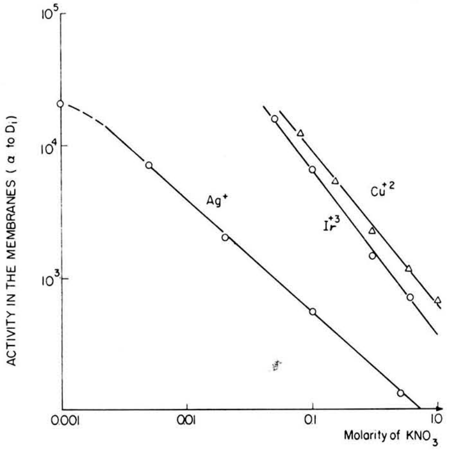

Figure 3. Dependence of distribution factor of trace ion on concentration of supporting electrolyte

Table II. Parameters Affecting Sensitivity of Ion Exchange Membranes as a Preconcentration Matrix for Neutron Activation Analysis

Parameter	Ag^{108}	Co^{60m}	Cu^{66}	In^{116m}
σ (cross section)	30	18	2.3	154
Abundance of parent, %	51.8	100	30.9	95.7
$t_{1/2}$, min.	2.4	10.5	5.1	54
γ-ray, M.e.v.	0.63	1.33	1.04	1.27
No. of disintegrations per 100 atoms activated	2	0.28	9	83

The ion exchange membranes can be used as a preconcentration matrix for direct irradiation because they are essentially pure organic in nature and, therefore, undergo no appreciable activation in themselves (Figure 4). Thus, the background activity from the matrix itself is very low.

For irradiation times less than 5 minutes the lower limit for the determination of Ag^+, in $0.01M$ KNO_3, is about $1 \times 10^{-6}M$; for Co^{+2}, $5 \times 10^{-6}M$; for Cu^{+2}, $5 \times 10^{-7}M$; and for In^{+3}, $2 \times 10^{-10}M$.

However, as the equilibration time required for concentrations less than $10^{-6}M$ is in the order of several days, such determinations are in general impractical.

In the analysis of biological materials or waste water, one encounters the problem of surface active agents. These tend to adsorb on surfaces and hinder processes such as electrodeposition and/or anodic dissolution—for example, silver ion in a supporting electrolyte of $0.1M$ KNO_3 and $1M$ NH_4OH saturated with the surface active agent 1-octanol, was investigated. The 1-octanol adsorbs strongly on the electrode in the potential range −0.1 to −0.9 volt *vs.* S.C.E. (Graham, 1946) and inhibits the electrochemical deposition process to such a

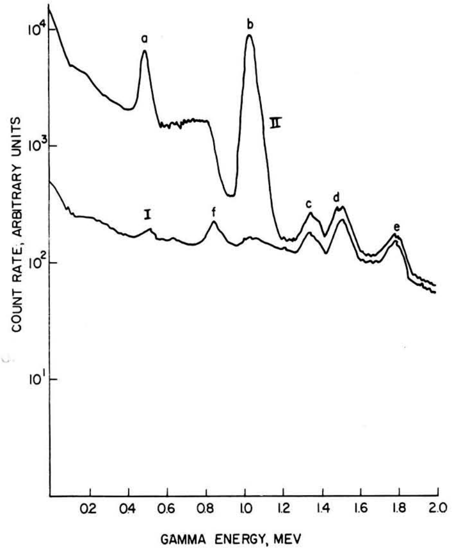

Figure 4. Gamma spectra of neutron-activated cation exchange membranes

I. Equilibrated in $0.1M$ KNO_3 II. Equilibrated in $0.1M$ KNO_3, 1×10^{-4} M Cu^{+2}, *a*. Cu^{64} 0.51-mev positron annihilation photopeak. *b*. Cu^{66} 1.04 mev. *c*. Na^{27} 1.37 mev. *d*. K^{42} 1.52 mev. *e*. Mn^{56} 1.81 mev. *f*. Mn^{56} 0.84 mev.

degree that no anodic peak is developed when normal anodic stripping voltammetry techniques are used.

To study the effect of surface active agents on the exchange process, membranes were equilibrated in the octanol–silver ion solution and in another solution which contained the same concentrations of all species excluding the 1-octanol. Activation analysis of the membranes themselves showed that both sets of membranes took up the same amount of silver, and calibration curves (activity in membrane *vs.* bulk concentration) for equilibrated membranes in silver solution in the presence of 1-octanol were linear in the range 4×10^{-5} to 15×10^{-5} (Figure 5). Thus, octanol does not constitute an appreciable disturbance in the ion exchange process and the equilibration time. (This means that surface active organic species present in all natural systems do not interfere with the direct activation analysis of these membranes.)

Application of Pre-equilibrated Membranes as a Preconcentration Matrix for Anodic Stripping Voltammetry. Silver ion concentrations in this concentration range were also determined using anodic stripping voltammetry with the membrane electrode assembly. A linear calibration of stripping peak area with bulk concentration of silver was obtained. The experimental procedure was as follows: Three membranes (for each sample solution) were equilibrated in the solution. After equilibration they were removed and washed with ethyl alcohol, followed by water to remove any octanol adhering to the membrane. The membranes were then mounted in the electrode assembly and electrolysis was carried out in a solution of base electrolyte alone (0.1*M* KNO_3 and 0.5*M* NH_4OH without surface active agent.) The dissolution step was then carried out in this same solution after removal of the membrane; ±5% accuracy was obtained.

The anodic stripping analysis, which is more laborious than direct activation of the pre-equilibrated membrane, was developed to determine species which do not have favorable cross sections, half lives, etc., for neutron activation analysis. Obviously, electrochemistry is only one of the possible analytical alternatives.

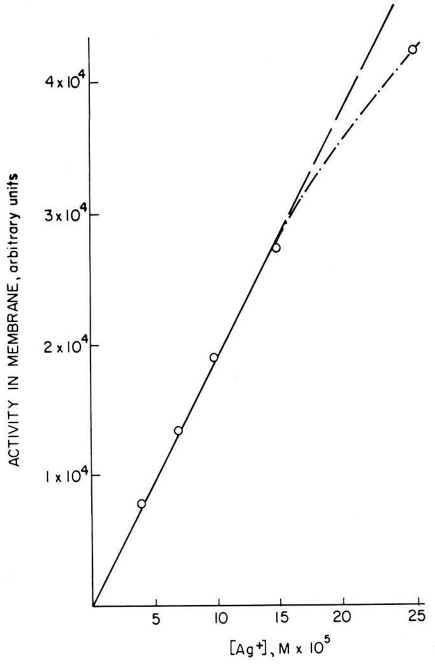

Figure 5. Calibration curve for silver in a solution saturated with *n*-octanol, supporting electrolyte 0.1*M* KNO_3

This method cannot be automatically applied to the analysis of any solution containing surface active materials, however, as one must ascertain if the surface active agent reacts with the ion under consideration. This can be illustrated by the following experiment with a solution containing $5 \times 10^{-5}M$ Cu^{+2} and 0.02% egg albumin. Equilibration of membranes in solutions containing various concentrations of copper ion showed a nonlinear relationship between concentration of copper in the membranes and in the solution. This indicates that the copper reacted with the albumin to form a complex.

The reaction of metal ions with proteins is well known. Many investigations have been carried out to determine the nature of reaction sites, the stoichiometry, and the structure of the complexes formed. The complexation of copper ions by albumin has been discussed (Gurd and Wilcox, 1956). A stoichiometric reaction of copper with bovine serum albumin in a NH_3-NH_4NO_3 buffer (pH 9.2) has been reported (Kolthoff and Willeford, 1957).

In the present case, the addition of 0.1*M* ethylenediamine to the solution yielded a linear relationship between the concentration of copper in solution and in the membranes. Equilibration of membranes in solutions containing $1 \times 10^{-4}M$ Cu^{+2}, 0.1*M* KNO_3, and 0.1*M* ethylenediamine, showed the same uptake of copper in the presence and absence of egg albumin, indicating that the copper ions were complexed only with the ethylenediamine. When ethylenediamine was replaced by NH_3, even in 1*M* NH_3, the concentration of copper in the membranes was 25% lower than in the absence of 0.02% albumin. The large difference in the formation constants of the two complexing agents accounts for the differences in the copper ion uptake (log K_1 for NH_3 4.27; for ethylenediamine 10.72) (Bjerrum, 1964).

Acknowledgment

The authors thank K. H. Mancy, Department of Environmental Health, School of Public Health, University of Michigan, for his interest in this work and his helpful suggestions. They are also indebted to the Michigan Memorial Phoenix Project for donating laboratory space and reactor time.

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COMMUNICATION

Determination of Odor Thresholds in Air Using C^{14}-Labeled Compounds to Monitor Concentrations

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■ The minimum identifiable odor levels of compounds in air were determined using a static dilution technique. Since adsorption of the compounds on the surfaces of equipment during the diluting procedures can potentially cause unknown and high errors, it is important to determine the true concentration in the air at the minimum identifiable odor level concentration. The authors do this by using C^{14}-labeled compounds and scintillation counting. Results for styrene, monochlorobenzene, and monochloroacetic acid are reported.

The determination of the odor threshold of a compound in air is subject to potentially high errors resulting from adsorption of the compound on the surfaces of apparatus and from diffusion losses. Of the two, the surface adsorption is probably of more significance, for both static and dynamic methods. The results leave doubt as to whether the concentration being inhaled is truly the concentration calculated from dilution ratios and known high concentrations. Of course, the lower the threshold, the more significant these sources of error can become. Thus, an acceptable value for a threshold concentration can be obtained only if a reliable analytical method is available. However, for compounds with very low thresholds, sufficient analytical sensitivity is often lacking and again surface adsorption makes it difficult to obtain and deliver an accurate aliquot of the system being tested for odor.

The authors, in studies on the odor threshold of various compounds in air, are using a static method and monitoring the low concentrations by using C^{14}-labeled compounds and scintillation counting. This overcomes the above-mentioned difficulties and allows the determination of a concentration in the threshold range regardless of how low this may be. Naturally, the quantities of vapor inhaled must be safe from the standpoint of toxicity.

Procedure and Apparatus

Preparation of Saturated Vapor. A saturated vapor in nitrogen is prepared in vessels similar to the one shown in Figure 1. The concentration is calculated and determined by gas chromatography or total carbon determination (Van Hall and Stenger, 1967). This saturated vapor is diluted by syringing portions directly into 12.5-liter inhalation flasks.

Panel Testing. The judge inhales this diluted vapor, using the nosepiece shown in Figure 2, which minimizes dilution with room air. Assuming the lungs hold 2 liters, the highest possible error would be approximately 15%, which is well within the range of individual sensitivities. Mixing is accomplished by having a 1 × 3 inch strip of aluminum foil (2-mil) in the flask and shaking the capped flask about 10 seconds. The

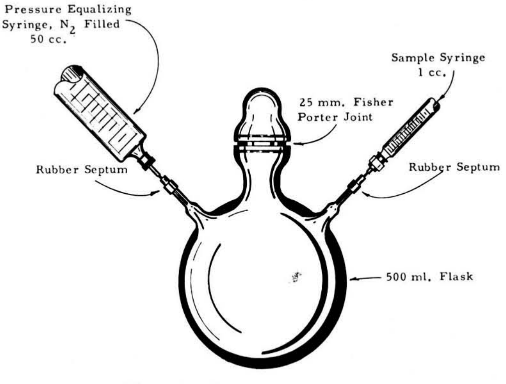

Figure 1. Saturated vapor flask

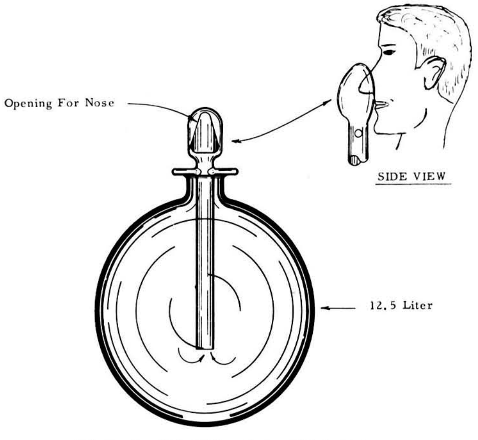

Figure 2. Inhalation flask with inhaling tube

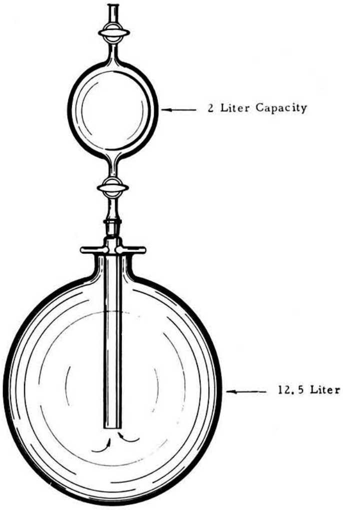

Figure 3. Inhalation flask with sampling unit attached

motion of the foil strip relative to the flask accelerates the mixing process. The inhalation test is made immediately after this mixing.

The end point is the recognizable odor threshold, commonly referred to as the minimum identifiable odor level (MIOL). This end point is used, at the present time, because the authors feel it is more meaningful than the absolute odor threshold for air pollution abatement studies. It represents the lowest concentration at which the odor of a compound can still be recognized as resembling the odor of the same compound at a much higher level, such as a saturated atmosphere at normal room temperatures. Differentiation from other similar compounds or odors is not considered. By this definition, then, other end points are possible, since some compounds do not retain all their primary odor qualities during dilutions, and the absolute threshold may not coincide with the MIOL.

A blank inhalation flask always accompanies the sample, for two reasons: to help monitor the flasks for odorless background, and to give the judge a point of reference. At the MIOL, the olfactory signal is so weak that often one has difficulty in mentally interpreting what the senses are detecting.

The sequence of sniffing the blank in respect to the sample is randomized. An experimental design allowing statistical analysis is not considered necessary for the MIOL determination, since the answer is definitely above the absolute threshold. The authors feel that when the MIOL is being approached by subsequent dilutions, a factor of one half each time is normally adequate. A panel of four men and three women is being used; and the final answer is reported as the panel average, panel range, and individual results. Testing is done in an atmosphere of charcoal-filtered air at 73°F. and 40 to 50% relative humidity.

Table I. Minimum Identifiable Odor Levels (MIOL)

Compound	Purity of Compound Inhaled, %	MIOL Panel Average, Mg./Liter	
		Theory	Scintillation counting
Styrene	99.6	3.4×10^{-4}	2×10^{-4}
Monochlorobenzene	99.9	4.3×10^{-3}	3×10^{-3}
Monochloroacetic acid	99.5	1.5×10^{-4}	5×10^{-5}

Monitoring MIOL Concentration. To correct for the probable adsorption and diffusion errors mentioned previously, compounds labeled with carbon-14 are diluted and then sampled using the 2-liter evacuated flask shown in Figure 3, and monitored by measurements of their radioactivity.

A concentration close to the panel MIOL average is monitored unless the panel range is broad, in which case the extreme values are monitored. The 2-liter aliquot in the sampling flask is transferred quantitatively to an appropriate counting solvent first by sweeping and then by rinsing the flask with the counting solvent. Counting is done on an automatic liquid scintillation spectrophotometer (Nuclear—Chicago Corp.).

Results and Discussion

Table I shows results for three compounds.

Compounds with sufficiently low activity, safetywise, can be used for the olfactory testing. However, the authors prefer to perform the olfactory testing on an unlabeled compound and run a parallel experiment with a labeled compound for concentration monitoring.

The results also indicate the magnitude of errors due to adsorption and diffusion.

Acknowledgment

The authors express their appreciation to L. E. Swim, L. E. Bartlett, and V. A. Stenger for their advice and assistance, and to M. E. Mandrell and J. Jewell for their assistance in obtaining and using labeled compounds and for the scintillation counting.

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Levels of Stable Strontium in Milk and the Total Diet

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■ Samples of pasteurized milk, composite total diet, and various other environmental media were analyzed for stable strontium, calcium, and strontium-90 during January through December 1965. These data are presented for use as reference material and interpreted with regard to significance of stable strontium levels. Pasteurized milk network samples from the southern United States, the Canal Zone, and Puerto Rico were analyzed. An average value of 0.86 ± 0.23 mg. of Sr^{2+} per liter was obtained for the 20 sampling stations. Values ranged from 0.43 ± 0.03 mg. per liter in Washington, D. C., to 1.51 ± 0.11 mg. per liter in Cristobal, Canal Zone. Composite total diet samples from children's homes in the southern United States were also analyzed. Individual stable strontium values ranged from 0.49 ± 0.02 mg. per kg. in Charleston, S. C., to 1.96 ± 0.10 mg. per kg. in Oklahoma City, Okla., with an over-all average of 0.89 ± 0.18 mg. per kg. wet weight.

For many years scientists have been aware of the presence of trace quantities of stable strontium in milk, food, and vegetation. However, the amount present was not considered important until the advent of radioactive strontiums as environmental contaminants. Beta-emitting strontium-90 is important from a health standpoint because of its long half life and bone-seeking characteristics, whereas strontium-89 is of less importance because of its much shorter half life. Stable strontium concentrations in the environment are important because of their influence on biological incorporation of the radioactive isotopes of strontium.

At the Southeastern Radiological Health Laboratory, pasteurized milk network and institutional total diet sampling network (radionuclide surveillance networks operated by the U. S. Public Health Service) samples were analyzed monthly during 1965 for stable strontium, strontium-90, and calcium. Various types of individual food, vegetation, and biota samples collected from certain areas of the southeastern United States were also analyzed on a random basis.

The stable strontium data are evaluated and an attempt is made to relate these data to radioactive strontium and stable calcium. Results are examined both individually and collectively as to sampling location and sample type, and seasonal trends and geographical variations are discussed.

The concentrations of stable strontium in environmental samples have often been neglected, partially because of the difficulty of determination (Elfers, Hallbach, *et al.*, 1964; Leddicotte and Reynolds, 1951) and partially because of the lack of emphasis on strontium prior to radiostrontium fallout.

The wide variations in the concentrations of stable strontium among sample types have shown that erroneous values for radiostrontium can result where the addition of stable strontium for the determination of chemical yield is part of the procedure. The presence of 1 to 5 mg. of natural stable strontium in a sample aliquot can produce significant errors, as the average amount of stable strontium carrier added is approximately 20 mg. (U. S. Public Health Service, 1967)

Sampling and Analytical Procedures

One milk sample per month from each of 20 pasteurized milk network (PMN) sampling stations (PHS regions III, IV, and VII) and one composite food sample (including dairy products) per month from each of seven institutional total diet sampling network (ITDSN) sampling stations were analyzed for stable strontium, stable calcium, and strontium-90. Samples from eight other ITDSN stations were also analyzed until these stations were discontinued after June 1965. The samples were analyzed for strontium-90 and calcium according to routine procedures in use at the Southeastern Radiological Health Laboratory (Porter, Augustine *et al.*, 1965). Stable strontium was determined by the ion exchange–flame photometric procedure described by Strong, Rehnberg, *et al.* (1968).

Results and Discussion

Table I contains values for stable strontium for 20 PMN sampling stations and 15 ITDSN sampling stations. From these data, average stable strontium values of 0.86 mg. per liter for milk and 0.89 mg. per kg. wet weight for food are calculated. Inasmuch as approximately 1 liter of milk or 1

Table I. Stable Strontium Concentration in PMN Milk (Mg./L.) and ITDSN Food (Mg./Kg.) Samples, 1965

		Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Yearly Station Averages
Washington, D. C.	PMN	1.10	0.81	0.64	0.53	0.74	0.73	0.66	0.68	0.81	0.43	0.50	0.49	0.68
Louisville, Ky.	PMN	0.97	0.59	0.82	0.62	0.71	0.64	0.59	0.82	0.48	0.57	0.53	0.49	0.65
	ITDSN	0.99	1.12	0.85	0.53	0.89	0.65	0.80	0.57	0.73	0.71	0.98	0.78	0.80
Baltimore, Md.	PMN	0.81	0.69	0.68	0.56	0.68	0.59	0.70	0.80	0.54	0.76	0.51	0.52	0.65
	ITDSN	0.59	0.77	0.85	0.77	0.67	0.81							0.74
Charlotte, N. C.	PMN	0.88	0.75	1.01	0.69	0.95	0.97	0.99	1.07	0.87	0.90	0.81	0.74	0.88
	ITDSN	0.67	0.89	0.87	1.03	1.02	0.87							0.89
San Juan, P. R.	PMN	0.89	0.64	0.77	0.49	0.84	0.88	0.62	0.96	0.63	0.59	0.49	0.47	0.69
Norfolk, Va.	PMN	0.80	0.68	0.86	0.66	0.46	0.72	0.71	0.90	0.77	0.62	0.58	0.44	0.68
	ITDSN	0.68	0.67	0.92	0.59	0.74	0.83							0.74
Charleston, W. Va.	PMN	0.72	0.80	0.88	0.62	0.63	0.70	0.71	0.78	0.75	0.63	0.53	0.49	0.69
	ITDSN	0.95	0.63	1.09	0.91	0.73	1.05							0.89
Montgomery, Ala.	PMN	0.63	0.85	0.96	0.73	0.93	0.85	0.76	1.21	1.31	0.73	0.83	0.69	0.87
	ITDSN	0.71	0.72	1.00	0.69	1.02	0.74							0.81
Cristobal, Canal Zone	PMN	0.83	1.12	1.38	1.04	1.17	1.19	1.18	1.27	1.51	1.51	0.94	0.82	1.16
Tampa, Fla	PMN	0.87	0.88	1.04	0.65	0.80	0.70	0.69	0.98	1.10	0.81	0.69	0.80	0.83
	ITDSN	0.86	0.97	1.10	1.25	0.82	1.06	0.89	0.74	0.92	0.76	1.08	0.78	0.94
Atlanta, Ga.	PMN	0.80	0.75	1.00	0.78	0.98	0.84	0.65	0.84	0.53	0.70	0.57	0.51	0.74
	ITDSN	0.94	0.99	1.42	1.01	0.94	1.09							1.06
Jackson, Miss.	PMN	0.73	0.94	1.35	1.08	1.09	1.02	0.96	1.24	1.28	0.91	0.79	0.95	1.03
	ITDSN	1.04	0.88		0.75	0.72	0.64	0.63	0.63	0.78	0.78	0.71	0.88	0.77
Charleston, S. C.	PMN	0.78	0.94	0.80	0.76	0.78	0.75	0.78	0.80	0.92	0.78	0.54	0.56	0.76
	ITDSN	1.23	0.79	0.88	0.49	0.62	0.58	0.61	0.63	0.73	0.74	0.63	0.74	0.72
Chattanooga, Tenn.	PMN	0.82	0.77	0.86	0.69	0.78	0.69	0.70	0.85	0.63	0.65	0.51	0.55	0.71
Memphis, Tenn.	PMN	0.71	0.75	1.37	1.02	1.04	0.89	0.81	1.30	1.25	0.81	0.77	0.75	0.96
	ITDSN	1.20	1.13	1.04	1.14	0.80	0.96							1.04
Little Rock, Ark.	PMN	0.70	0.72	1.13	0.96	0.70	0.94	0.88	1.08	1.08	0.65	0.64	0.77	0.95
	ITDSN	0.95	0.64	1.05	0.84	1.06	0.99	0.68	0.60	0.85	0.71	0.77	0.91	0.84
New Orleans, La.	PMN	0.78	1.03	1.30	1.22	1.10	1.18	1.25	1.31	1.21	0.87	0.74	0.86	1.07
	ITDSN	0.74	1.12	1.21	0.77	1.18	1.01	1.03	0.84	0.96	0.79	0.88	0.69	0.94
Oklahoma City,	PMN	0.79	1.01	1.40	0.97	1.09	1.12	1.10	1.19	1.28	0.96	0.88	0.89	1.06
Okla.	ITDSN	1.96	1.61	1.53	1.66	1.65	0.93							1.56
Austin, Tex.	PMN	0.88	1.15	1.40	1.06	1.31	1.20	1.19	1.43	1.40	1.35	0.86	0.89	1.18
	ITDSN	0.64	0.84	0.96	0.78	0.74	0.77	0.86		1.12	0.85	0.96	0.98	0.86
Dallas, Tex.	PMN	0.74	1.10	1.28	1.15	0.99	1.01	1.16	1.01	1.20	0.88	0.82	0.85	1.02
Iowa	ITDSN	0.88	0.83	0.98	0.57	0.82	0.70							0.80
Kansas	ITDSN	1.21	0.93	1.25	1.31	1.14	1.20							1.17
Monthly	PMN	0.81	0.85	1.05	0.81	0.89	0.88	0.85	1.03	0.98	0.80	0.68	0.68	0.86
Average	ITDSN	0.95	0.92	1.06	0.89	0.92	0.88	0.79	0.67	0.87	0.76	0.86	0.82	0.89

kg. of food is the size of sample aliquot usually used in radiostrontium analysis, this amount (approximately 1 mg.) of stable strontium in a sample to which 20 mg. of strontium carrier had been added could create an analytical error of 4 to 5%.

A comparison of stable strontium in PMN milk samples and in ITDSN composite food samples is presented in Table II. From the average percentage of milk contained in ITDSN samples, the average weight and per cent of strontium contributed by milk were calculated. The per cent of stable strontium contributed by milk to these composite foods ranges from 21 to 60.

No correlations between strontium-90 and stable strontium concentrations are apparent in either ITDSN or PMN data.

Figure 1, however, shows an apparent rise in strontium-90 values in the spring and autumn months, with a possible rise in the stable strontium values. This spring and autumn rise in strontium-90 concentrations has been noted previously (Federal Radiation Council, 1964).

Strontium-calcium ratios are presented in Figure 2. In 1959, Alexander and Nusbaum proposed a linear correlation between the strontium-calcium ratio in bone and in milk (Alexander and Nusbaum, 1959). Using six areas in the United States they calculated this ratio to be 0.18 ± 0.05, where milk contributes 75% of calcium to the human bone. Reports by the United Nations Scientific Committee on the Effects of Atomic Radiation (1962, 1964, 1966) supported this conclusion. The United Nations Committee on a worldwide basis used 0.25 for the strontium-calcium ratio in bone and in the diet. Using these ratios, it is possible to predict the strontium-calcium ratio in bone at each of the PMN or ITDSN locations included in this report. Using PMN data an average ratio for bone was determined to be 0.23 mg. of Sr per gram of Ca; a value of 0.32 mg. was calculated using ITDSN data. Both estimations are well within the range of values previously published (Alexander and Nusbaum, 1959; Bryant, Chamberlain, *et al.*, 1958).

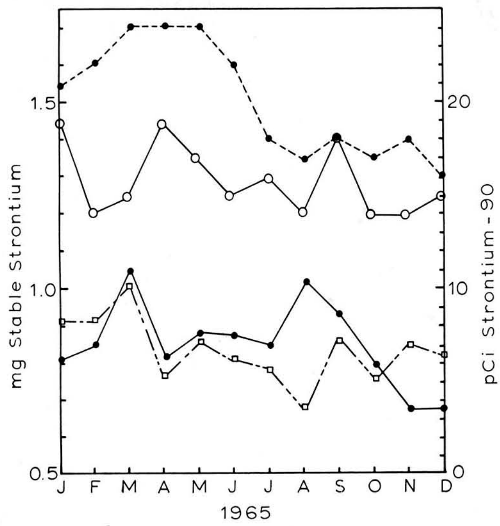

Figure 1. Strontium-90 and stable strontium in ITDSN food and PMN milk samples

Monthly averages
●- - - -● PMN, pCi ^{90}Sr/liter
○—○ ITDSN, pCi ^{90}Sr/kg.
●—● PMN, mg. Sr/liter
□— - -□ ITDSN, mg. Sr/kg.

Table II. Stable Strontium in PMN Milk and in ITDSN Food Samples

	ITDSN Food, Mg./Kg.	PMN Milk, Mg./L.	Milk in ITDSN Sample, %	Sr in Food Contributed by Milk Mg.Sr/Kg. Food	%
Alabama	0.81	0.87	25	0.22	27
Arkansas	0.84	0.85	36	0.31	37
Florida	0.94	0.83	40	0.33	35
Georgia	1.06	0.74	30	0.22	21
Kentucky	0.80	0.65	34	0.22	28
South Carolina	0.72	0.76	40	0.30	42
Louisiana	0.94	1.07	34	0.36	38
Maryland	0.74	0.65	36	0.23	31
Mississippi	0.77	1.03	45	0.46	60
North Carolina	0.89	0.88	23	0.20	22
Oklahoma	1.56	1.06	40	0.42	27
Tennessee	1.04	0.96	29	0.28	27
Texas	0.86	1.18	25	0.30	35
Virginia	0.74	0.68	23	0.16	22
West Virginia	0.89	0.69	39	0.27	30

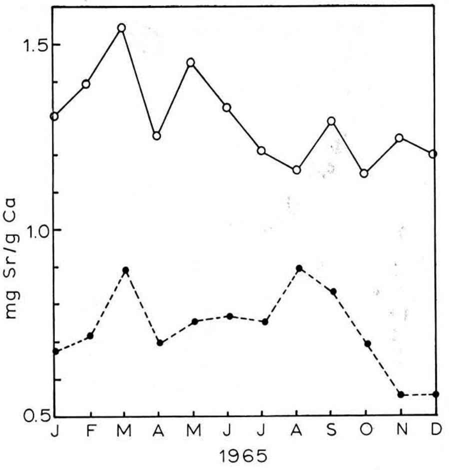

Figure 2. Ratio of strontium to calcium in ITDSN food and PMN milk samples

○ ITDSN
● PMN

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Book on water-use economics rates high

The Economics of Water Utilization in the Beet Sugar Industry. George O. G. Löf and Allen V. Kneese. ix + 125 pages. Johns Hopkins Press, Baltimore, Md. 21218. 1968. $4.00, paper. *William Whipple, Jr., is Director, Water Resources Research Institute, College of Agriculture and Environmental Science, Rutgers, The State University, New Brunswick, N.J. 08903.*

By William Whipple, Jr.

"The Economics of Water Utilization in the Beet Sugar Industry" is a welcome instance of economists getting down to cases with a real water resources problem. The authors have made a serious attempt to determine factually, for the beet sugar industry, the consumption of water, and, much more important, the costs of controlling the quality of waste water discharge to any given degree. The work is clearly written, and, obviously, represents a real effort to obtain and present the facts. Although based upon a single rather unglamorous industry, the conclusions have important policy implications for the entire field of industrial pollution control.

This report is not likely to attract a large public. The technology of the beet sugar industry, even clearly and accurately described, is rather heavy going for the general reader. Outside of managers of the industry, the greatest appeal will be to individuals—mainly in the government and the universities—who have a real understanding of, and interest in, the economics of water pollution. Unfortunately, this group is not very large. The conclusions deserve a wider public and probably will reach that public ultimately in much simpler form embodied in other works, without substantiating detail.

The authors go to considerable pains to establish the background of technology in the beet sugar industry, the various processes, how those processes affect the usage of water and the wastes created, and the process changes over a period of years which have reduced both water withdrawals and the amount of waste produced. The quantity of waste produced is measured by biochemical oxygen demand (BOD). Although other pollutants exist in effluents, BOD is the most serious.

Actual water consumption in the beet industry is not very great, although it has been increasing in recent years, and cannot now be determined accurately. As in the case for most other industries, the principal economic cost entailed by water usage is the resulting pollution in the waste water. A single average plant (there were 58 plants in the industry in 1962) produces gross wastes of about 40,000 lbs. BOD daily, which is said to represent the equivalent of raw sewage from a city having a population of about 270,000. After treatment, the total is reduced from 40,000 lbs. to about 15,000 lbs. This is a much lesser degree of treatment than usually would be considered acceptable for municipal sewage. Therefore, from the organic pollution viewpoint, a beet sugar plant is a really major source of stream pollution.

Reduction in industrial pollution

The authors state that, reportedly, the European industry produces only from one half to one quarter the organic pollution per ton of beets processed, as is the case in America. Obviously, a much greater reduction in industry pollution would be feasible; and the key effort of the book is to determine the costs of doing so. The principal ways of improving quality of effluent are by recirculation of process water and its attendant treatment, pulp drying, modern methods of processing Steffens waste, and re-use of condenser water, as well as specific waste treatment processes.

For the entire industry, if there were absolutely no requirement for limitation of wastes, the authors estimate that the long-term savings to the industry would be about $2 million annually below present costs. On the other hand, to eliminate nearly all beet sugar wastes from surface streams, a much larger investment would be required, with total costs approaching $5 million annually. This larger investment is about 1% of the gross industry income of $500 million or one seventh of annual net profits. The shape of the cost curve is particularly significant. Unit costs of eliminating successive increments of BOD vary from about $1 to about $90 per pound of BOD removed.

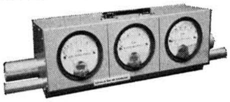
In the book, the authors show a hypothetical damage function curve, with a hypothetical optimal point where the incremental damage caused by pollution would be balanced by the incremental costs of removing that pollution. However, as the authors are well aware, this part of the analysis must remain hypothetical for the time being, since the methods of evaluating economic damage caused by poor water quality are just beginning to be developed.

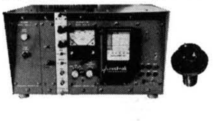
The following two final general conclusions are well substantiated by the evidence:

- Projections of water and waste loads which are made by applying coefficients based upon present technology to projected industrial production are not reliable, since changes in technology can very materially change the coefficients. Because such projecting is a usual practice among planners, this conclusion has considerable importance.
- Economic incentives offered industrial firms to treat their waste (as by tax abatement) may lead to grossly inefficient measures, since changes of process rather than waste treatment may be a better way of handling the problem. The authors comment on research needed as to treatment methods for the wastes which process modification cannot be expected to eliminate. The research aspect is important, because the sugar in the wastes is apparently somewhat difficult to handle by biological process.

Concept of BOD

From the viewpoint of scientific treatment control, the criticism may be made that the concept of BOD is handled a little loosely. The questionnaires distributed refer to "BOD removal" without specifying further. Presumably, such data as were returned were given in terms of 5-day BOD, as commonly measured. At one point the statement is made that BOD reductions due to pond retention times of





from one to five days are "almost entirely due to the settling of suspended matter." This could be true if there were substantially no biological action on the sugars during this period. But, this situation could be verified only through relatively sophisticated methods of measuring ultimate BOD. If normal 5-day BOD measurements do not decrease after a detention period of several days, it may be that there has been no biologic consumption of organic material during the period. Alternatively, it may be that the BOD-time curve is not of the shape which is normal for carbonaceous BOD. The authors' statement indicates that the retained wastes are not normal in this respect; but the use of the term BOD with no further explanation leaves it unclear what the situation actually is.

Another technical deficiency is the apparent failure to realize that the ponding of highly polluted effluents can affect water supplies through underground seepage, even where no effluent flow escapes on the surface. In the discussion of water use, the authors estimate that underground seepage averages from 15–17% of all withdrawals compared with 6–17% consumed by evaporation. Obviously such concentrated wastes, characteristic of the beet sugar industry, can produce very serious pollution of aquifers and adjacent streams.

There was one rather startling statement that the condenser water had a rather low BOD concentration—about 40 p.p.m. This concentration is many times higher than BOD normally expected of condenser water. However, in this case referred to by the authors, the condenser includes a spray which entraps vapors that have a considerable content of sugar. The 40 p.p.m. is only low with respect to other wastes common in the industry.

However, the objective of the authors was primarily economic; and these technical aspects do not have an effect sufficient to reduce the value of the main conclusions reached. In any event, much of the material was received from questionnaire and interview and must be regarded as approximate. In the area of water pollution, the situation is usually so poorly defined that approximations of this nature can be of considerable value.

From the viewpoint of public policy, the conclusions of the book relate to one major point which the authors do not comment upon. The effort involved to determine costs of controlling pollution in this one industry would have much more significance if the hypothetical pollution damage curve were to be evaluated. Knowing that various increments of organic pollution can be eliminated at costs per pound starting at $1.00 and increasing gradually to $90.00, one cannot help feeling that somehow there should be a determination of the value of eliminating various degrees of organic pollution from our streams. If this were done, the usefulness of studies such as this would be greatly increased.

In order to eliminate flagrant abuses, and initiate a national program without delay, water quality standards in streams have been generally established without quantitatively economic evaluation. The authors' conscientious attempt to evaluate cost factors of controlling waste in one industry is a step toward the economic evaluation of water quality, and warrants particular attention for this reason. ■

A Major Program of Water Resources Research in Canada. Report No. 3. 37 pages. Queen's Printer, Ottawa, Canada. 1968. $.75, paper.

Believing that research into Canada's water resources is important to the nation, the Science Council of Canada assigned a study group to assess activities in water resources and research. The publication presents the findings of the group and the recommendations made by the Science Council to the Prime Minister. ■

Water Resources Research in Canada. Special Study No. 5. J.P. Bruce and D.E.L. Maasland. xvi + 169 pages. Queen's Printer, Ottawa, Canada. 1968. $2.50, paper.

The publication is the result of a technical study sponsored by the Science Secretariat, to determine the status of research on water in Canada. A special report by W.R. Derrick Sewell, on the contribution of social science research to water resource management is included. The status of Canada's water resources and problems in this area are discussed, as well as types and benefits of research in the field. The authors also present a summary of their major recommendations, a list of tablets, and an appendix containing abstracts of background studies submitted by four consultants engaged by the Science Secretariat. ■

Proceedings of the Sixteenth Southern Water Resources and Pollution Control Conference. Edited by Edward H. Bryan. vi + 181 pages. Department of Civil Engineering, Duke University, Durham, N.C. 27706. 1967. $5.00, paper.

The conference, held April 6-7, 1967, at Duke University, was jointly sponsored by Duke, North Carolina State University at Raleigh, and University of North Carolina at Chapel Hill. The publication contains more than 20 papers dealing with technical, legal, and political aspects of waste water treatment, pollution control, and impact of pollution on water resources. Topics discussed at the meeting include: informed public—the key to water resources conservation; people, politics, and pollution; reuse of plant effluent as process water; and oxidation ponds and tertiary treatment—performance as a function of retention time. ■

Air Pollution Control. Volume 33, Law and Contemporary Problems. 230 pages. Duke University School of Law, Duke Station, Durham, N.C. 27706. 1968. $3.00, paper.

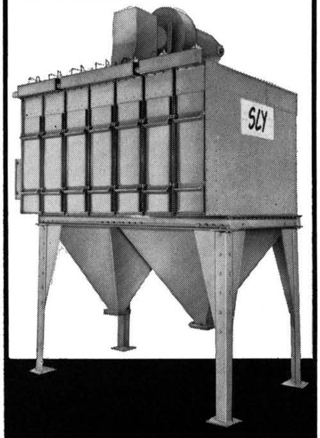
The publication presents the papers of a symposium on air pollution control, sponsored by the Duke University School of Law. Economics of air pollution, a guide to the Air Quality Act, deficiencies in the act, as well as legal boundaries of control are among topics discussed in detail. ■

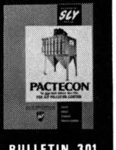
The Weather Bureau and Water Management. 16 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1968. $.25, paper.

Published by the U.S. Department of Commerce's Environmental Science Services Administration, the illustrated brochure describes the facilities and services of the Weather Bureau for river, flood, and water supply forecasting. These and other hydrological services provided by the bureau are essential for navigation activities, pollution abatement, fish and wildlife management, industrial practices along rivers, reservoir operation, and a score of uses affecting the environment. ■

Planning and Cities. Edited by George R. Collins. George Braziller, Inc., One Park Ave., New York, N.Y. 10016.

An illustrated series on the history of urbanization, "Planning and Cities" explores the major epochs in the history of cities and the planning of environment from biblical times to the present. The series is organized into groups, the first of which is historical. Subsequent groups will discuss theoretical concepts in planning, lives and projects of great planners, and roles of various professional disciplines in planning. Each volume is illustrated with photographs, plans, maps, and drawings, and authored by historians interested in architecture as social art. Four volumes are available:
Village Planning in the Primitive World. Douglas Fraser. 128 pages. 1968. $5.95, hard cover; $2.95, paper.
Cities and Planning in the Ancient Near East. Paul Lampl. 128 pages. 1968. $5.95, hard cover; $2.95, paper.
Urban Planning in Pre-Columbian America. Jorge Hardoy. 128 pages. 1968. $5.95, hard cover; $2.95, paper.
Medieval Cities. Howard Saalman. 127 pages. 1968. $5.95, hard cover; $2.95, paper. ■





new products digest

Undersea Measurements

The Model TDC Metering System is the first of a line of instruments for use in marine science education. The manufacturer claims that the portable instrument—consisting of transistorized readout module, multiconductor underwater cable, and remote multielement sensor—is capable of simultaneous measurement of marine temperature, depth, and conductivity. The system is designed for instructional use in classroom, laboratory, or at sea, and can be operated by inexperienced technicians or students. Martek Instrument, Inc. **61**

Better Tasting Water

A small appliance-style water purifier makes it possible to transform poor quality, bad tasting water into sparkling delicious water in the kitchen, for as little as 7 cents per gallon, according to the manufacturer. Operating on the reverse osmosis principle, the Aqua I Water Purifier features a purifying membrane, requires no electrical connection, processes 56 gallons of water per day, and may be installed on or under standard kitchen wall cabinet, wet bar, or any convenient wall where a water line is available. The unit rejects cloudiness, sediment, undissolved minerals, organic matter, detergents, bad taste, odors, offensive colors, and even chlorine in water. Culligan, Inc. **62**

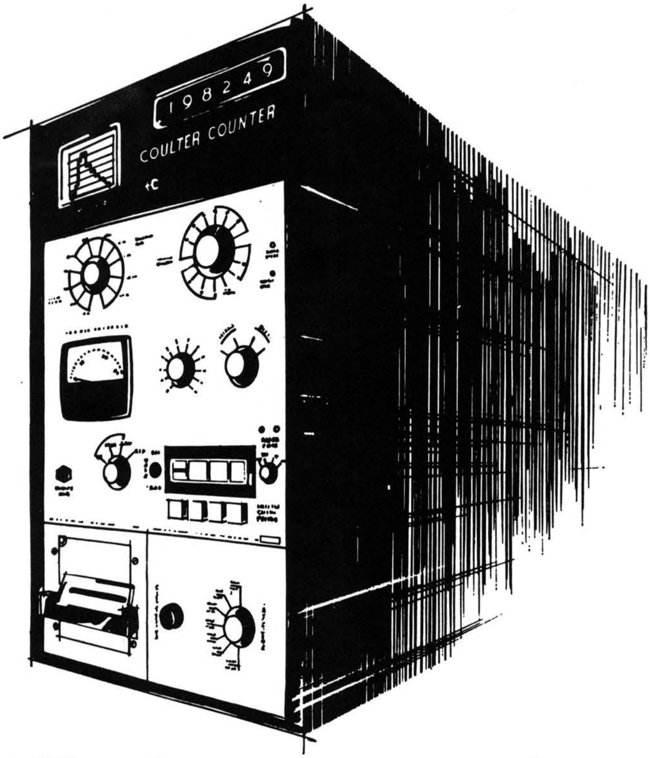
Computerized Analysis

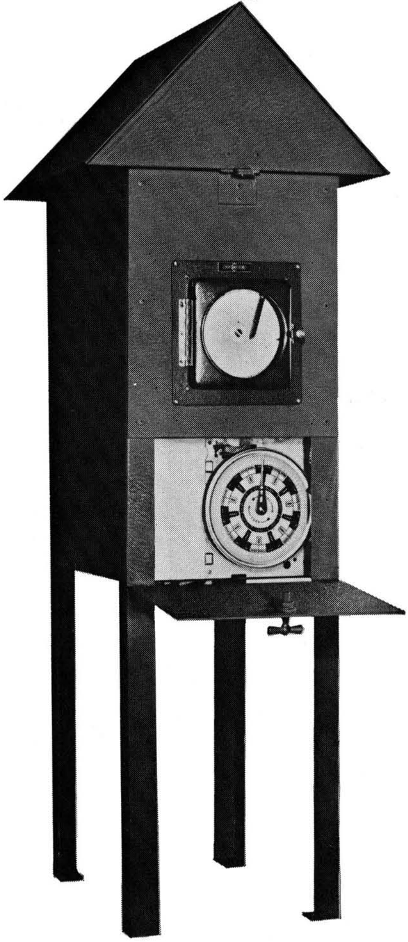
An automated system for continuous on-stream monitoring of up to 26 gases is available. The system fea-

tures simultaneous output of quantitative and qualitative data in the control of water and air pollution, and can be operated by a plant foreman or technician. Five key elements make up the system: gas sampling and vacuum system; quadrupole residual gas analyzer used as sensing component; automatic data aquisition center, compact digital computer; and computer programming. This gas analysis system is modular, with specific configurations engineered for application requirements. Varian Assoc.
63

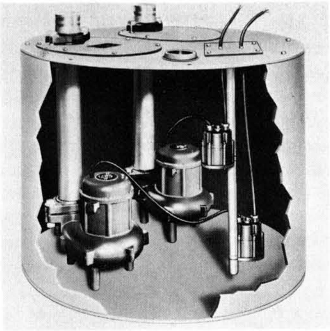
Gas Detectors

A line of devices for detection of hydrocarbon gases including methane, as well as alcohols, ketones, ethers, etc., are available. All units of the line operate on the natural diffusion principle, requiring no tubes, pumps, or sampling systems. The Model 1100 G, a hand-held combustible gas detection gun, is designed for personal protection in remote areas, as well as for use in plant installations, detection of fuel storage leakage, and boat engine compartment monitoring. Operating on rechargeable batteries, the unit features a test switch for automatic warning at weakening of battery signal, and an alarm to warn of gas concentrations from 0–100%. The Model 70 units form a system which can be expanded as needs increase in rack-mounted, multichannel configurations, to provide continuous positive detection. When gas accumulations rise above the preset lower alarm level, a green light is extinquished and an amber warning light goes on—if concentration continues to rise, a red light flashes and audible signal is given. Both alarm points (set from 0–100%) have relay closures available for operation of control or shutdown devices.





The units are suitable for plant locations and sites where continuous detection is desired. General Monitors, Inc. **64**



Sewage Pumps

A line of submersible sewage ejector pumps features a level sensor submersible switch which eliminates need for exposed controls on tank cover plates; nonclog performance; cast iron impellers, volutes and motor housing, according to the manufacturers. Available individually or as systems, the pumps have application in commercial, industrial, and household waste disposal. Fairbanks Morse **65**

Particulate Detection

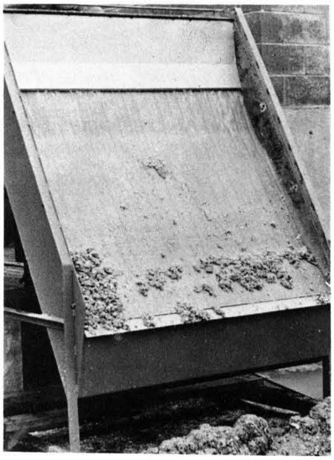
Precision instruments which provide continuous instant analog readout of aerosol particle concentration and size are available in two models (Clean Room Particle Counter and Air Pollution Particle Counter). The transistorized solid-state automatic Particle Counters utilize the light scattering technique and feature adjustable full-scale deflection, optional chart speeds, field calibration, and compact, lightweight design. The manufacturers claim the devices can continuously display and record number of particles per cu. ft. in the size ranges 0.5 micron and larger, and 5 microns and larger. In addition, they feature analog readout and a 2-pen chart recorder. Gelman Instrument Co. **66**

Airborne Particle Detector

Featuring an elliptical mirror optical sensor which detects and sizes particulate matter by the forward light scattering technique, the CI-201/207 Particle Analyzer/Counter/Printer counts, displays, and accurately records airborne particle concentration, according to the manufacturer. The unit, designed for long-term studies, can be programmed to automatically sample the atmosphere, providing printed summations of particles counted at intervals from a few seconds to one hour. Each printout contains date, hour, and minute of the sample, as well as the number of particles counted in each of two size ranges—0.5 micron and larger, and 5 microns and larger. Climet Instruments, Inc. **67**

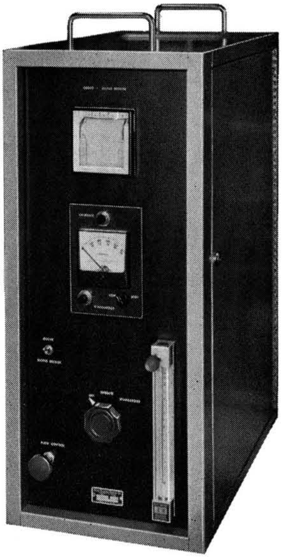
Dual Column Chromatography

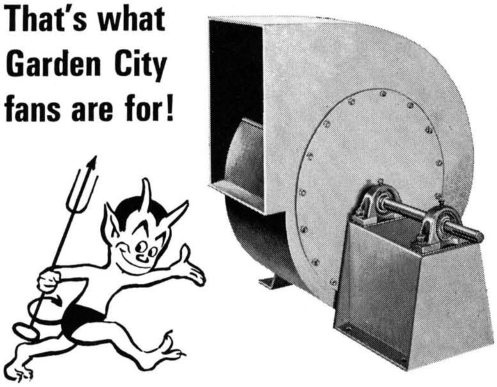
The Model 15C-3 Dual Column Isothermal Gas Chromatograph for use with automatic data reduction systems is available. The unit features basic dual column flow system, permitting sample introduction into either of two columns, two columns simultaneously, or two columns in series with a detector at the end of each. Optional features include automatically or manually operated sample valves, back flush valve, or column switching system. Loenco, Inc. **68**

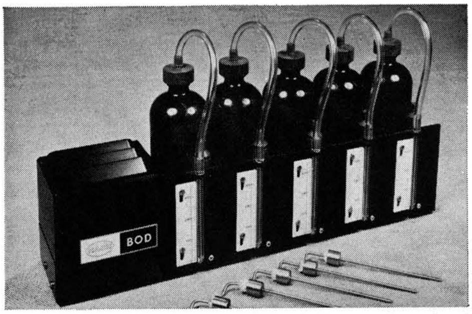


Solid Waste Removal

A device for removal of coarse suspended solids from waste treatment plant influent operates by drawing particulate matter out from under the carrier water, thus reducing the load to sludge digestion facilities. The Elimin-Ator, constructed of stainless steel, features sloping transverse bars, which form a grid ranging in 5 widths from 18–72 inches. The manufacturer claims that the unit—which is self-contained with no motor or moving parts—provides BOD removal comparable to primary settling, is nonclogging, and provides minimum pump clogging and digester scumming. Designed for use in sanitary sewage treatment, the device has application in meat rendering, pulp and paper, and other industries. Welles Products Corp. **69**







new literature digest

Pipe line filters. Nine basic models of pipe line filters for plant service are described in a 4-page illustrated brochure (GP 2001). The nine basic designs are available in 300 variations, for uses that include protecting pneumatic tools, instruments, precision controls, vacuum pumps, pneumatic handling systems, gas regulators, and gases or air at all pressures and temperatures, anywhere they must be kept clean and dry. The brochure also lists specifications for the filters and operating ranges for each model. Dollinger Corp. **91**

Turbidity measurement. A new 8-page, 4-color brochure on Model 2100 Laboratory Turbidimeter discusses turbidity, principles of operation of turbidity meters, and the operating values of the specific meter itself. The instrument has changeable meter scales, wide-range capability, extreme sensitivity, trouble-free operation, and is easy to standardize, the company says. Hach Chemical Co. **92**

Gravity filters. A 2-page, 2-color bulletin (646) provides information on a line of gravity filters for industrial and municipal water supplies. The filters are available in flow rate ranges from 14–236 g.p.m. Also in the bulletin are features on type of construction and standard components that come with the units. Elgin Softener, Inc. **93**

Flotation machines. A 2-page bulletin briefly discusses the flotation process, changes in flotation machine design, and new developments that offer the chance to reduce operating costs. The bulletin also describes two basic types of flotation machines (cell-to-cell and free-flow). Denver Equipment Co. **94**

Pollution control report. Directed at the subject of plating wastes, this 12-page report has been designed to serve as a reference source and to provide general information on current techniques used to handle the wastes generated during electrolytic plating operations. The report covers the major techniques which include recovery, dilution, and ion exchange. Ritter-Pfaulder Corp. **95**

Pyrolysis for IR analysis. In a 6-page booklet "Don't Fight It, Burn It," some examples and discussions are presented to show the time-saving techniques of pyrolyzing obstinate samples for infrared analysis. Also included in the booklet are reproductions of various spectra of samples prepared by pyrolysis for IR analysis. Barnes Engineering Co. **96**

Exhaust purifiers. Information is available from the company on their full line of purifiers for gasoline, liquid propane gas, and diesel engines. The purifiers use a honeycomb catalyst that has operating life expectancy of 5000–10,000 hours and that—under normal operating conditions—removes up to 96.5% of all carbon monoxide, 98% of all smoke, and 99% of all odors from engine exhaust. Oxy-Catalyst, Inc. **97**

Reverse osmosis membrane. Bulletins TMB-1 and -2 describe the special features of the Eastman membrane that make it suitable for reverse osmosis and other related uses, and present a bibliography of membrane technology. The membrane, available in full production quantities, is made in a two-step process that yields a very thin (0.25) but dense continuous skin of cellulose acetate over one side of a porous substructure. Eastman Kodak Co. **98**

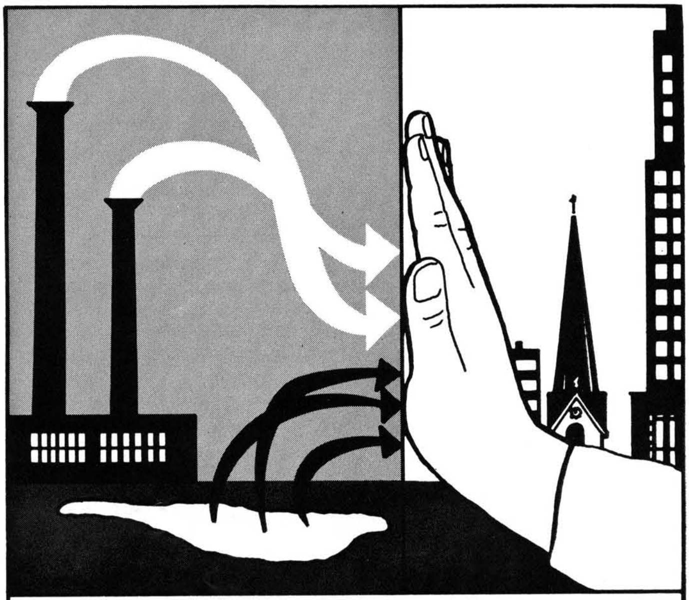
Electronic instruments. A pocket-sized 48-page comprehensive directory to Beckman's major electronic instruments, services, and sales and service offices is available. Included in the booklet are sections that provide technical reference data, purchasing information, and lists of the major product lines and capabilities of the entire company. Beckman Instruments, Inc. **99**

Plating waste controls. A 12-page pamphlet describing three basic methods—continuous destruction, closed loop ion exchange, and, evaporative recovery—for treating plating wastes is available. The pamphlet includes process flow diagrams and other data relevant to solving metal finishing waste treatment problems. Permutit Co. **100**

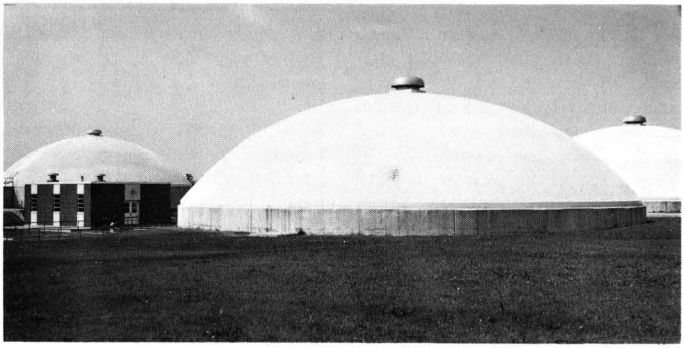
Low flow indicators. A new 4-page technical bulletin (DS-1510) describing a series of low cost, low flow rate indicators is available. The devices are suitable for applications that do not require great accuracy, such as cooling water flow indication. Emerson Electric Co. **101**

Solvent recovery. A 4-page technical bulletin describes a solvent recovery system that uses activated carbon to recover such materials as ketones, esters, alcohols, and hydrocarbons, among others. The systems permit the recovered materials to be reused and, at the same time, help the cause of air pollution abatement. Also included in the bulletin are a flow diagram, a list of recoverable solvents, and data on the lower explosive limits of various solvents. Vulcan, Inc. **102**

Laboratory supplies. A new 55-page catalog describes a line of gas chromatography supplies, thin-layer chromatography adsorbents and equipment, high purity lipids, and new products manufactured by the company. Catalog No. 12 also provides an index to materials as well as ordering information. Applied Science Laboratories, Inc. **103**



Processing unit domes. Designed to cover trickling filters, clarifiers, and other circular structures, these domes, made of plastic foam and latex-modified cement, are discussed in a 12-page, 4-color brochure. The domes, which can be constructed on the site, serve to improve efficiency, enhance appearance, and contain odors when used on waste water processing units. The brochure offers some design criteria, and includes photographic coverage of construction and installation. Dow Chemical Co. **104**

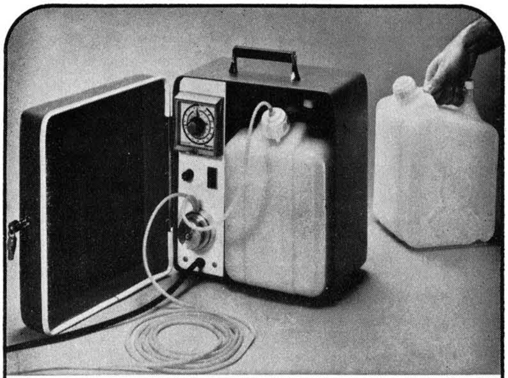


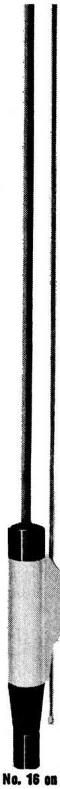
Ion exchange resins. Duolite Data Leaflet No. 3 describes—in chart form—a line of regenerated ion exchange resins. The 4-page catalog details properties and performance data of the resins, which the company says can meet any military and commercial specifications. Diamond Shamrock Chemical Co. **105**

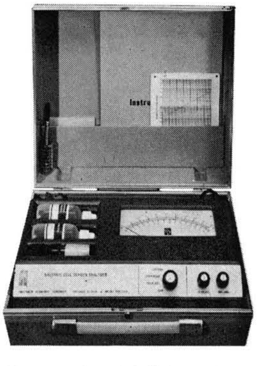
Strip photo printer. A solid-state continuous strip printer for geological surveying highway and city planning, aerial reconnaissance, forestry management, bulk inventory control, and water and air pollution control or surveillance is the subject of a new 2-page technical bulletin. The printer, which compensates for varying densities in the negative, enhances photographic information by automatic modulation of the light used to expose the printing material. LogEtronics, Inc. **106**

pH Analysis. An 8-page bulletin (4088) describes the Model 900 pH Analyzer. The company claims that the instrument gives continuous pH or ORP analysis in a variety of applications including sewage and waste water treatment, power generation, mining, food processing, and chemical manufacture. Specifications and information on electrodes, electrode chambers, and other accessory equipment is included. Beckman Instruments, Inc. **107**

Chlorinated hydrocarbon pesticides. "Occurrence and Significance of DDT and Dieldrin Residues in Wisconsin" is the result of a 3-year survey to determine the amounts of DDT and dieldrin in a variety of fishes found in various Wisconsin waters. The 43-page report—Technical Bulletin No. 41—presents the information gained





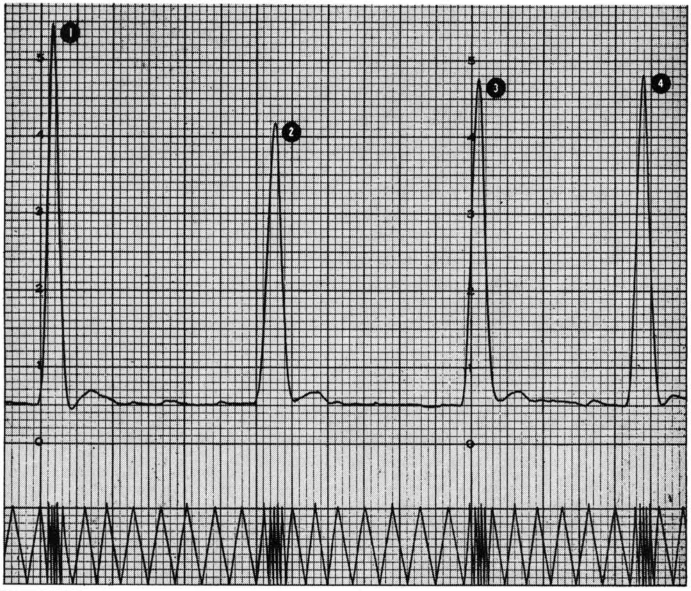


as well as discussion of the significance of the collected data. A perspective section is included to orient the reader to the nature of the two pesticides studied, acquainting him with the use, movement and accumulation in the environment, concentration in fish, and general toxicity of the insecticides. Department of Natural Resources, Madison, Wis. 53701. (Write direct)

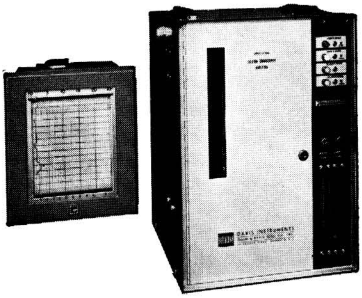
Antilitter campaign. A 16-page booklet, "Litter-Prevention . . . An Aid to Conservation"—distributed as a public service by Shell Oil Co.—discusses litter as a national disgrace, health menace, and costly eyesore, and also examines other aspects of the problem. In addition, the book outlines what the public—from vacationing family to seasonal sportsman—can do to improve conditions in the nation's parks, beaches, recreation spots, and other areas where the public gathers. Keep America Beautiful, Inc., 99 Park Ave., New York, N.Y. 10016. (Write direct)

Polluted air. "The Physician's Guide to Air Pollution" is a 20-page booklet designed to provide current information on this environmental health problem to the physician, the medical society, the community, and to voluntary health and scientific organizations. The book presents a definition of pollution, examines the sources of air pollution and methods of containing them, and describes a medical program necessary to meet the opportunities and challenges open to the physician in order to meet the requirements of air resource management. American Medical Assoc., 535 N. Dearborn St., Chicago, Ill. 60610. (Write direct)

Processing solid wastes. Methods of processing solid wastes into compost are the subject of Report SW-2c, "Solid Wastes Management/Composting; European Activity and American Potential." The 40-page report (PHS publication No. 1826) is a result of a study on the status of composting and compost utilization in Germany, Holland, and Switzerland. Findings were related to the solid wastes problem in the U.S., and specific recommendations made for research to define the economics and technical aspects of composting which may serve to promote the practice of this technique in the U.S. Environmental Control Administration, U.S. Public Health Service, 222 E. Central Pkwy., Cincinnati, Ohio 45202. (Write direct)



Effective air pollution surveys depend on Davis SO_2 Detectors



Public health services, air pollution departments and private industry* rely upon the high sensitivity of Davis Model No. 11-7010 Recording Type Sulphur Dioxide Detector. It may be used in laboratory or mobile unit, even a helicopter. High sensitivity range 0-1 P.P.M. SO_2 in air, threshold approximately 0.05 P.P.M. Easily operated and maintained — needs no chemicals. Available with pyrolizing furnace for H_2S detection and inverter for battery-operated mobile use. **Write for Bulletin No. 5070.**

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General Electric Co.
Mt. Vernon, Indiana
Design: Did engineering design for 3 million gallon-per-day municipal-type water treating system for chemical plant on Ohio River.

Bareco Wax
Kilgore, Texas
Analysis, Design, Construction: Constructed facility for separating oil and paraffin material from waste brine stream. Drilled waste disposal well for injection of brine; built incinerator for disposal of oil and paraffin materials.

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March 2-5
Wildlife Management Institute
34th North American Wildlife and Natural Resources Conference
Washington Hilton Hotel, Washington

Having as its central theme, "Conservation in an Urbanizing Society," the 4-day meeting will cover all phases of restoration and management of natural resources. Technical sessions include discussion of coastal and marine resources; disease, nutrition, and control; measuring wildlife values; and forest and range resources.

March 7-8
City of Santa Clara and San Jose State College
Symposium of Improved Municipal Solid Waste Collection and Disposal Practices
Hotel St. Clair, San Jose, Calif.

Topics for discussion at the meeting include: solid waste master planning, incineration, accelerated refuse decomposition and stabilization, and landfill equipment evaluation. In addition to these technical sessions, the symposium will feature a series of related field demonstrations.

March 9-11
National Service to Regional Councils
3rd Annual Conference of Regional Councils
St. Francis Hotel, San Francisco

Informational workshops covering regional issues and programs will be the main component of the three-day conference. Scheduled for discussion are solid waste disposal programs; air pollution control; economic and resource development; and the role of private enterprise. In addition, experimental decision-making sessions and consultation sessions will be important parts of the meeting.

March 19
University of Cincinnati Medical Center
Colloquium on Man and His Urban Environment
Tangeman University Center, Cincinnati, Ohio

Conducted as part of the University of Cincinnati Sesquicentennial Celebration, the one-day meeting will feature speakers who will discuss those urban habitats which alter the quality of man's environment, and assess current aspirations for improvement of these conditions, and the prospects for achieving such upgrading.

March 24-27
Clapp & Poliak, Inc.

20th Plant Engineering & Maintenance Conference

Convention Center, Cleveland, Ohio

This year's conference will feature a session devoted to air pollution, and one dealing with water pollution. A discussion of air pollution control equipment in Cleveland will highlight one meeting; the water session will consider the controlled disposal of plating wastes and control of water pollution. For further information: Clapp & Poliak, Inc. 245 Park Ave., New York, N.Y. 10017

April 7-11
Southwestern Radiological Health Laboratory, Public Health Service

Symposium on Public Health Aspects of Peaceful Uses of Nuclear Explosives

Frontier Hotel, Las Vegas, Nev.

The six sessions of the meeting will consist of more than 35 papers on such topics as environmental health and safety aspects in the event of large-scale use of nuclear explosives for peaceful purposes; roles of industry, Atomic Energy Commission, Public Health Service, and states.

April 9-11
North Carolina State University, Duke University, and University of North Carolina

Southern Water Resources and Pollution Control Conference

North Carolina State University,
Raleigh, N.C.

The conference is designed to bring together representatives of industry, government, universities, and consultants to discuss water, utilization, and waste disposal in the southeastern U.S. Meetings will examine new treatment techniques, and designing and operation of treatment facilities for water utilization and waste disposal. For further information, contact: Maynard Shields, P.O. Box 5125, Raleigh, N.C. 27607.

April 13-16
Water Conditioning Association International, and Illinois Water Conditioning Association

Water Conditioning Management Institute

University of Illinois

Aimed at dealers and management personnel, the institute will include marketing, organizational performance, sales management, finances, and communications. Limited enrollment. For information: Box 651, 325 Wesley St., Wheaton, Ill.

April 20-23
Institute of Environmental Sciences

15th Annual Meeting

Disneyland Hotel, Anaheim, Calif.

"Man in His Environment" is the topic of the technical sessions of the meeting. In addition to presentation and discussion of papers, research development, application and management advances in environmental stimulation will be covered. Topics for discussion include the general areas people, pollution, noise, transportation. For information: Frank Hallstein, Technical Program Chairman, TRW Systems, 1 Space Park, R-5/2063, Redondo Beach, Calif. 90278.

April 21-24
Industrial Medical Association, and American Association of Industrial Nurses

American Industrial Health Conference

Shamrock Hilton Hotel, Houston, Tex.

The conference will encompass the 54th annual meeting of IMA and 27th annual meeting of AAIN In addition to conferences and discussions of industrial and occupational health topics, the conference will include a number of field trips, a medical TV program, and a series of postgraduate seminars. Among topics for discussion are atmospheric contaminants and standards, underwater medicine, how to solve an environmental health problem in industry.

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April 21-25
International Association on Water Pollution Research
4th International Conference on Water Pollution Research
Prague, Czechoslovakia

The technical program of this meeting, rescheduled from September 2–6, 1968, features 48 papers in three sections: stream pollution; waste water treatment; and lakes, reservoirs, and the ocean. In addition, there will be a panel discussion on the reuse of water, and a technical film festival on water pollution subjects. Additional information can be obtained from: Dr. T. G. Shea, International Association on Water Pollution Research, Room 114 McLaughlin Hall, University of California, Berkeley, Calif. 94720

April 22-24
Houston Junior Chamber of Commerce
National Pollution Control Conference and Exposition
Astrohall, Houston, Tex.

Environmental Equilibrium: Criteria, Cost, Cooperation is the theme of the 3-day conference, which aims to provide a forum for exchange of information on government regulations regarding pollution, technological advances, and subjects of general interest in pollution abatement. For additional information, contact: Aubrey LaFargue, c/o Pace Management Corp., 4710 Greeley St., Houston, Tex. 77006.

April 28-30
Technical Association of the Pulp and Paper Industry
6th Water and Air Conference
Robert Meyer Hotel, Jacksonville, Fla.

Five technical sessions are planned for the conference, as well as tours of water and wastes facilities at area pulp and paper mills. Papers will be presented on water supply and treatment; re-use of water; waste water and sludge treatment; instruments; and air conservation. Inquiries should be directed to: H. O. Teeple, TAPPI, 360 Lexington Ave., New York, N. Y. 10017.

Courses

March 11-14
Instrument Society of America
Short Course on Fundamentals of Dynamic Measurements as Applied to the Ocean Sciences
LeBaron Hotel, San Diego, Calif.

Designed for practicing engineers, scientists, and technicians who use sophisticated instrumentation in ocean research, the four-day course attempts to enhance their knowledge of the instruments necessary to perform measurements of time-carrying phenomena as thev apply to ocean sciences. At least one half of the course will consider experimental techniques of specific interest to the ocean researcher.

March 24-28
University of California, Berkeley
Short Course on Desalination: Methods and Applications
College of Engineering, University of California, Berkeley

The 5-day course is planned as an introduction to the subject of desalination, as well as a survey of the state of the art, covering the development, theory, application, and economics of the principal methods of desalination. For details: Continuing Education in Engineering, University Extension, University of California, 2223 Fulton St., Berkeley, Calif. 94720.

June 2-7
Manhattan College and the Federal Water Pollution Control Administration
14th Summer Institute in Water Pollution
Manhattan College, Bronx, N.Y.

Two simultaneous one-week courses will be offered for advanced study in stream and estuarine analysis and biological waste treatment. Stipends and travel allowance are available for U.S. citizens associated with universities and state regulatory agencies. For information: Donald J. O'Connor, Civil Engineering Department, Manhattan College, Bronx, N.Y. 10471

Special Notices

June 9
American Board of Health Physics
Examination for Certification
Selected cities

Applications must be submitted by April 1 for admission to the two-part written examination. Applicants must have at least 6 years' professional experience beyond the bachelor's degree, and present supporting statements from supervisors and coworkers, as well as records of experience and training. Those health physicists having only 2 years' experience may apply for admission to Part 1 of the exam. For forms and details: Dade W. Moeller, Kresge Center for Environmental Health, Harvard School of Public Health, Boston, Mass. 02115.

June 30
Environmental Engineering Intersociety Board
Qualifying Certification Examination
Various locations

In addition to satisfactory completion of an oral and written examination, requirements for certification include good moral and professional character, a degree in engineering from a qualified institution, registration as a professional engineer in the U.S. or Canada, and 8 years of professional environmental engineering work. Each applicant certified becomes a member of the American Academy of Environmental Engineers. Applications must be received by April 1, 1969. For further information: Frank A. Butrico, P.O. Box 9728, Washington, D.C. 20016.

1969-1970 Academic Year
University of Colorado, Boulder

Federal Water Pollution Control Traineeships

Financial assistance is available for graduate study in water resources and sanitary engineering. Applicants with a background in engineering or science will be considered for the grants. Annual stipends for master's candidates are $2400 per year plus $500 per dependent. Those interested in graduate programs in water resources engineering or the chemical and microbiological aspects of water resources should contact: Director, Water Resources Program, Engineering Center OT 4-34, University of Colorado, Boulder, Colo. 80302.

1969-1970 Academic Year
University of Florida Department of Environmental Engineering

Environmental Research Program in Terrestrial Ecology

Applications will be accepted for admission to a program of environmental research in tropical and subtropical terrestrial ecosystems. Emphasis of the project-oriented program is on the team approach, combining such specialists as agronomists, ecologists, entomologists, and the like, with environmental engineers, health physicists, and radiochemists. Research topics are available at the master, doctoral, and post-doctoral level. Contact: Terrestrial Ecology Research Program, Department of Environmental Engineering, University of Florida, Gainesville, Fla. 32601.

1969-1970 Academic Year
Harvard School of Public Health

The Kresge Center invites candidates to submit applications for enrollment and fellowships for study leading to the M.S. and D.Sc. in occupational medicine, environmental physiology, toxicology, aerospace health and safety, radiological health, air pollution control, industrial hygiene, and general environmental health. Fellowship stipends range from $200–300 per month, with $500 per year for each dependent, plus full tuition and fees. For details: Dr. Dade W. Moeller, Assoc. Dir., Kresge Center for Environmental Health, Harvard School of Public Health, 665 Huntington Ave., Boston, Mass. 02115.

1969-1970 Academic Year
University of North Carolina, Institute for Environmental Health Studies

Environmental Health Fellowships

Applications may be filed for fellowships which provide tuition, fees, and a stipend, including a dependency allowance. Fellowships are available for masters or doctoral candidates, as well as for postdoctoral studies. Recipients participate in multidepartmental programs designed to prepare students for careers in research, teaching, and practice in the various specialized fields in environmental health. For details: Institute of Environmental Health Studies, Box 630, Chapel Hill, N.C. 27514.

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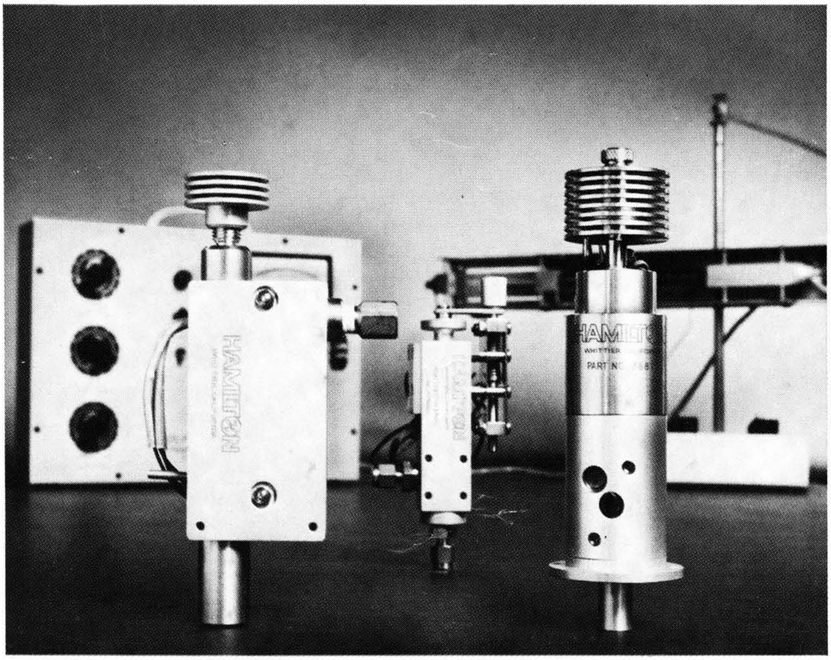
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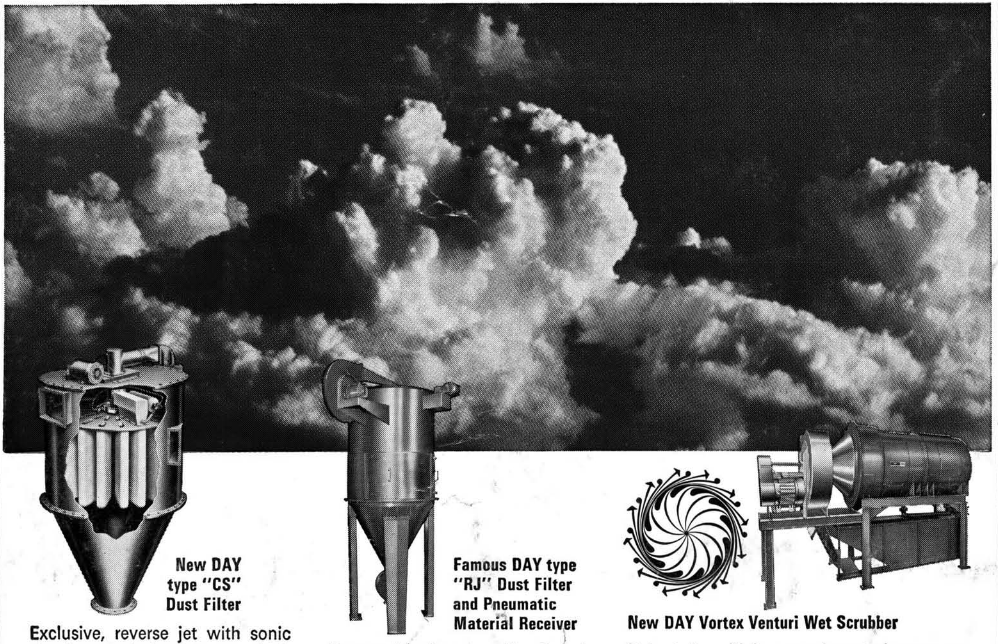

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