ENVIRONMENTAL
Science & Technology

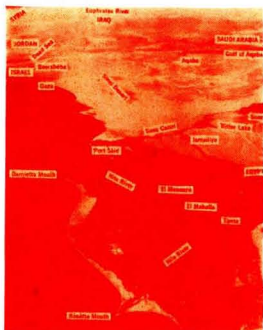*Emphasizing*

Water,

Air, &

Waste

Chemistry

JUNE 1967

This is one drop
of water
beyond
our control.

GATX admits it.
We haven't got the answer to this problem.
We don't know anyone who does.
But there are plenty of water treatment problems we can help you control.
We'll help you clear up the water with Infilco   water treatment systems.
We'll help you store water by designing and constructing storage tanks
     for its conservation.
We'll help you clean up the air, too. Dracco dust collecting systems will
     make a clean sweep of most industrial dust and gas problems.
In fact, we can fabricate and erect the entire water or air pollution control
     installation for you.
So when you're thinking about cleaning up our environment, look up GATX.
We know enough to humble ourselves before some problems.
And we're wise enough to help you solve others.

GENERAL AMERICAN TRANSPORTATION CORPORATION, CHICAGO

GATX ™

ENVIRONMENTAL
Science & Technology

CONTENTS

Series 700 Laboratory GC's are custom-assembled for your <u>present</u> need yet capable of <u>future</u> modification···at a budget price

Sometimes you just don't need all the capability that's built into an expensive research type gas chromatograph. That's when the F&M Series 700 Laboratory GC may be your best buy. Order it equipped only with the features that you need for your current analytical program. Later you can modify your 700 to suit the needs of a new program, by ordering from a large number of interchangeable detectors and accessories.

The primary advantage is financial—Series 700 prices start at $1100. Yet the 700 is a modern dual-column instrument with on-column injection, high-temperature operation to 400°C, separate temperature control of oven and detector, and temperature programming capability.

There is no sacrifice in flexibility because the 700 is a modular instrument with a full line of inter-changeable detectors (dual thermal conductivity, dual flame ionization, electron capture with tritium or with our new Ni^{63} source for operation up to 355°C, and micro cross-section). Also, a long list of custom-fitted accessories to suit almost any application is available (flow controllers, rotameters, linear temperature programmers, liquid, solid and gas sampling accessories, recorders, integrators, attenuators).

You can get the full story by writing for Bulletin 7000-3. Or call the nearest H-P sales office.

Hewlett-Packard, F&M Scientific Division, Route 41, Avondale, Pennsylvania 19311. In Europe: Hewlett-Packard S.A., 54 Route des Acacias, Geneva, Switzerland. Elsewhere: Hewlett-Packard Export Marketing, 1501 Page Mill Road, Palo Alto, California 94304.

HEWLETT PACKARD **hp** F&M SCIENTIFIC DIVISION
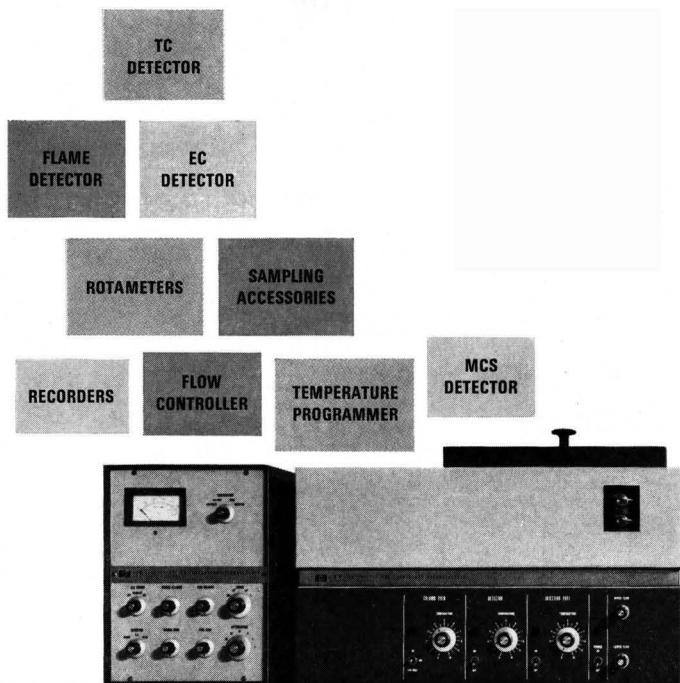
43705

EDITORIAL

Government has major role in environmental management

Interested citizens and industry have an obligation to help in the formation of efficient and effective programs

Increasingly responsive to the demands of an aroused citizenry, government at local, state, and national levels continues to broaden the base from which it plans attacks on environmental problems. And, according to a recent National Academy of Sciences report to the House Committee on Science and Astronautics, government has a special responsibility for the integrity and sufficiency of man's environment. Whatever the motivation—political power, the higher good, concern for present and future generations—politicians will continue to press for programs and controls that are directed at environmental management.

Following on the heels of the NAS report was HEW's Task Force on Environmental Health and Related Problems report, *A Strategy for a Livable Environment*. The task force report calls for stringent government controls in all matters of environmental problems ranging from stack and vehicular emissions, to where people should be allowed to build homes, or what new synthetic materials industry should be allowed to make and sell.

What these two reports suggest—indeed, what governmental actions and official statements affirm—is that government involvement will become greater because "the environment impinges so extensively and inescapably on the lives of all citizens and transcends so generally all private spheres of influence."

The private sector of our society could have taken the lead in developing action programs and goals, but it did not. Government moved, and continues to move, to fill the gap. Nonetheless, there is time for the private sector to get in on the action and to present meaningful and effective comments and suggestions on government programs. Although it does not seem probable that the private sector will ever be able to assume a principal leadership role in environmental management, there is no reason why it cannot assume an active statesmanship role.

To this end, industry must prove that it recognizes its responsibility in contributing to the problem and tell clearly the story of what it is doing to mitigate the effects. Further, industry must continue to make known and available the skills, technologies, and facilities it has to accomplish the cleanup.

Private citizens, alone or in concert, must do more than react to a fait accompli. They must make themselves aware of the problems and needs so they can put their informed imprint on the direction and extent of environmental management programs.

The private sector has a vital stake in the evolution of environmental management programs, because, as Senator Edmund Muskie (D.-Me.) says, we can expect "more restrictions on the use of materials and equipment, planning, development and land use in our modern complex society. It will be costly. But the price must be paid."

Melvin J. Josephs

Now, a complete
water quality program.

Measure 1, 2, or any 12 water pollutants...automatically, continuously and specifically.

You may want to quantitate COD, phenols, cyanide, ammonia nitrogen, or any one of a host of pollutants. You may even want to quantitate 12 at one time. Technicon® AutoAnalyzer® systems, employing Standard Methods, give you this flexibility, as well as accuracy and specificity. Around-the-clock watch on vital water quality measurements can be returned within 15 minutes. Low maintenance enables a network of these monitors to be established at extremely low cost. The Technicon brochure CSM-12 explains how the limitation of exactly measuring the many possible pollutants is removed by continuous on-site monitoring. Write for it. Dept. G, Technicon Corporation, Ardsley, New York 10502.
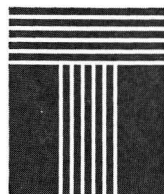
Circle No. 22 on Readers' Service Card

Government Has Special Environmental Role

Government has a special responsibility for the integrity and sufficiency of man's environment—this is one of the main conclusions of a report just presented to the House Committee on Science and Astronautics. Prepared by a National Academy of Sciences panel, *Applied Science and Technological Progress* consists of 17 "criticized essays" which examine American applied sciences. Preston E. Cloud, Jr., and V. E. McKelvey, in their paper point out the need for the government's involvement because "the environment impinges so extensively and inescapably on the lives of all citizens, and transcends so generally all private spheres of interest."

Private industry, they believe, can be involved to a limited extent by appropriate appeals, rewards, and penalties. Pollution abatement is a good example of a problem set for which government should explore use of such incentives. Industrial laboratories are oriented to production and operations and, hence, are best suited to engineering and development activities, Cloud and McKelvey say. Universities will continue to train environmental scientists and, therefore, to maintain a modest research effort. The universities seem to do best with free-wheeling innovative research not tied to specific missions.

Government establishments are best suited to undertake long-continuing, comprehensive mission-oriented research and surveys. The quality of the government's operations in the environmental sciences ranges from outstanding to substandard, according to Cloud and McKelvey. "Principles of good science- and engineering-management are not uniformly applied." The result, they say, has been to weaken the effectiveness of some agencies.

The report also touched on the need to go beyond the simple identification of broad problem areas—for example, pollution—if effective control programs are ever to evolve. Specific problems for which technological solutions seem possible must be identified, according to the report, and the decisions for procedures and priorities should be established by technically trained people.

Vinyl Liner Helps Reduce BOD Level More Than 90%

Du Pont is just putting the finishing touches on a vinyl lined aeration pond that the company claims is the largest of its kind in the world. The six-acre pond has a capacity of 21 million gallons and is part of a new waste disposal system that will effect more than a 90% reduction in the BOD flowing into nearby streams at the company's Photo Products plant in Parlin, N.J. The plant currently discharges 2.5 to 3.0 million gallons of water containing 2000 pounds of BOD per day. The water discharge rate will remain the same, according to company officials, but the pond and related facilities will reduce the BOD content to less than 100 pounds. Here, workers are pulling the 20 mil-thick light blue vinyl liner into place.

Recommendations from Eutrophication Symposium

Eutrophication is an increasingly urgent problem, but the problem and the urgency to solve it are poorly understood. This is one of the conclusions of the International Symposium on Eutrophication (Madison, Wis., June 11–16). The symposium's planning committee recommended that an information program be instituted to inform the general public about how lakes and streams age and—more importantly—about how man's activities speed up this aging.

By dumping in sewage, industrial wastes, and agricultural fertilizers, man adds nutrients that hasten both the natural and gradual processes. The committee suggested that federal, state, local, and private agencies undertake large-scale demonstration projects to evaluate various approaches to controlling eutrophication. The committee also called for more multidisciplinary research to help provide understanding of the mechanisms, processes, and consequences of eutrophication. (For a detailed discussion of eutrophication of Lake Erie, see ES&T, March, page 212. See also letters in ES&T, May, page 446, and this issue, page 516.)

"The significance of industrial and municipal waste effluents has been re-emphasized at the symposium," the committee said. "At the same time, reports given at the conference have made us more keenly aware of the potential importance of animal wastes in contributing to the eutrophication problem." The recommendations are being sent to the National Academy of Sciences–National Research Council, which sponsored the symposium. The planning committee will meet this summer to draw up more recommendations based on the symposium.

Muskie on Air Pollution Legislation

The Air Quality Act of 1967 will probably differ in a key provision from the Administration's original proposal. As the Senate Subcommittee on Air and Water Pollution prepares to start drafting the bill, chairman Edmund S. Muskie (D.-Me.) seems ready to abandon the idea of national emission standards. At the convention of the National Coal Association this month he came out for a control program which would "take maximum advantage of existing technology on a 'where needed' basis, emphasizing the protection of health and welfare, with a gradual tightening of requirements for environmental improvement as technology advances."

Muskie admits this approach may not fully satisfy the slogans of "Clean Air Now." But, warns Muskie, air pollution control may require "more severe restrictions on the use of materials and equipment, planning, development and land use in our modern complex society. It will be costly. But the price must be paid."

ES&T Lends a Hand

Data for such national air monitoring programs as National Air Sampling Network and Continuous Air Monitoring Program are gathered at a variety of stations throughout a metropolitan area—near heavy traffic, in industrial areas, near apartment building incinerators, and the like—and then averaged to present an overall picture of a city's pollution levels.

Recently the American Chemical Society, through ES&T, became host to four small devices for gathering data on pollution: a 24-hour high-volume particulate sampler, a 2-hour AISI particulate sampler, an ozone determinator, and a sulfur dioxide sampler. Here, John Holmes (left) and Charles Brunot (right), Air Pollution Division of the Department of Public Health, government of the District of Columbia, start operation of the monitoring equipment on the rooftop of the ACS headquarters building (Washington monument in background).

HEW Task Force Calls for Stringent Controls

Although air, water, and land resources are limited, the number of Americans is growing, and their affluence and effluents are increasing. HEW's John W. Gardner established the Secretary's Task Force on Environmental Health and Related Problems last November 16 to study health hazards in our environment. This month the group released its report, *A Strategy for a Livable Environment*, which contains among its 34 recommendations suggestions for alleviating such widespread problems as air and water pollution, solid waste disposal, noise, crowding, radiation, and traffic safety.

The study group proposed 10 action goals, each with a date for accomplishment: for example, plant stack and vehicle exhaust emissions should be reduced 90% by 1970, and all public water systems tested by the same date. The effect of population trends on environmental health goals should be studied, and housing, urban development, and transportation regulated by 1969. New synthetic materials should be prohibited until approved by HEW, hazardous consumer products must be controlled, and occupational disease protection and safety measures must be uniformly enforced throughout the nation.

The task force suggests a national Council of Ecological Advisors, similar to the President's Council of Economic Advisors, which would eliminate the fragmentary approach so often taken in environmental matters. And, for those recommendations requiring legislative action, the group proposes a well publicized Environmental Health Act, to be submitted to Congress by the President. Such a clearly identifiable package will promote public awareness of environmental health problems, as well as facilitate passage of the act, the task force says.

EROS—An Overview of the World We Live On

With its Earth Resources Observation Satellite, the Department
of Interior plans to find out a lot more about our natural resources
and use the facts to improve the quality of our environment

Almost 300 satellites are circling the earth today, according to estimates of the National Aeronautics and Space Administration. By 1970 there will probably be more; at least one of them—if Interior Department plans are fulfilled—will be EROS, the Earth Resources Observation Satellite. Designed specifically to gather data on natural resources, EROS offers scientists a unique opportunity to take a long and penetrating look from afar at our planet.

For more than a quarter of a century, Interior has been using remote sensing—sometimes defined as telling something about something without actually touching it—to study resources problems. During the past four years, Interior has worked intensively with NASA on aerial surveys of selected sites in the U.S. From these surveys, Interior learned more about how to apply some of the new, space age, sophisticated sensors to resources problems. Interior also came to feel that remote sensing from spacecraft was superior for many purposes to remote sensing from aircraft.

Gemini photographs dramatically demonstrated this superiority. In three minutes, for example, the astronauts photographed almost 80% of Peru. A mosaic of the photographs is better than any available map of the region, Interior Secretary Stewart L. Udall said recently. "One can see the gross patterns of land use, distribution of snow, the levels of the lakes, geologic features of possible economic significance—all at a single glance."

Space sensing has other advantages:

• At higher altitudes, some things can be seen better than at lower altitudes. For example, it is possible to see farther into bodies of water from space. Thus, space sensing would help in studying the resources of the Continental Shelf, or in determining the buildup of silt in reservoirs.

• At greater speeds, satellites can record changing phenomena. On one of

Joshua Tree National Monument

Coachella Valley
Salton Sea
Imperial Valley
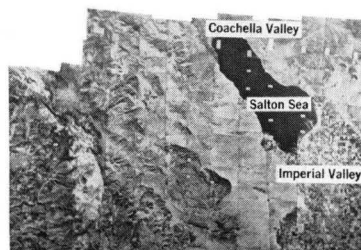
Infrared. *Special camera systems in satellites can be used to provide data on such things as geothermal power sources or vegetative cover. On this page a normal photo; on the opposite page a photo from an infrared sensitive camera shows high temperature areas in the crater and flanks of Kilauea Volcano in Hawaii*

Halemaumau
Kilauea Iki
Panchromatic photograph
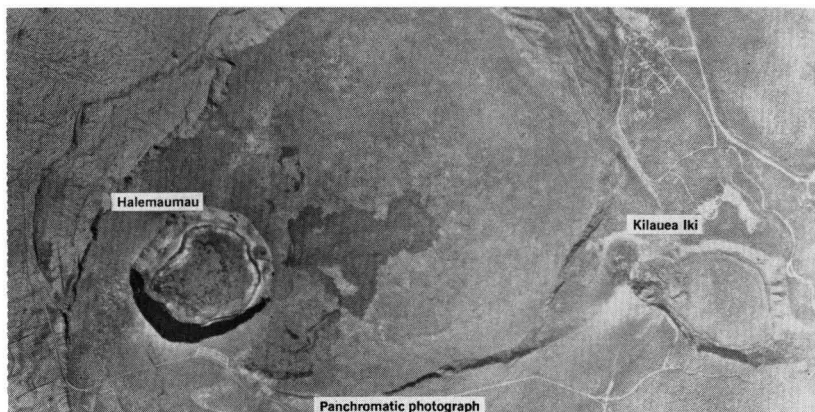
its flights, Gemini photographed an entire storm pattern covering hundreds of square miles. The pattern would have disappeared before an aircraft could have recorded it.

• Comparative data at a uniform scale can be obtained all over the earth. Also, the number of individual pieces of data collected is reduced. For example, to get a picture of the entire U.S. a conventional aircraft would take 1.5 million photographs versus 400 for a spacecraft.

• Costs are lower than for aerial sensing. Space sensing is less for the first coverage of a large area, and it gets less and less expensive for each successive coverage. In contrast, aerial costs remain constant for each coverage. Repetitive coverage is particularly important in hydrology, geography, and agriculture, where workers want to observe changes with time.

In planning a systematic program of space sensing, Interior expressed its needs for resource data to NASA. And the two are now working together to fill these needs:

• An earth-orbiting satellite that can last at least a year (to catch all seasons).

• A narrow-angle camera that can see through greater depths of water.

• A higher-resolution camera that can get greater detail.

Last fall, Interior revealed its plans for EROS: an unmanned satellite to be launched by a Thor Delta booster into a near-polar, sun-synchronous orbit. A 30° sun angle was selected as being best for looking at terrain. Cost: in the order of $20 million. Target date: 1970. "Prospects are good for our meeting that date," says W. A. Fischer, research coordinator of the EROS program.

Interior's Geological Survey has been placed in charge of the EROS program. Initially, says Fischer, the program will stress cartography, geography, geology, hydrology, and the marine sciences—the sciences in which USGS and Interior are primarily interested. But space sensing could also be used in all the sciences concerned with natural resources, including meteorology, agriculture, fish and wildlife management, and land management.

USGS has set these specific goals for its first satellite:

• Examining the configuration of the earth, including underwater features.

• Determining the distribution of water, both as free water and as moisture.

To accomplish these goals, the satel-

One versus many. *A mosaic (left) of more than 500 aerial photos is needed to cover the same area as shown in the single Gemini photo (right). Swirl in Gemini photo of the Salton Sea reveals water dynamics not seen in the mosaic aerial photo*

Space surveys are effective and efficient		
Number of times area is surveyed	Space photography	Aerial photography
	Cost per 100 square miles	
1	$25.00	$ 500
2	12.50	1000
3	6.25	1500
4	3.12	2000
5	1.56	2500

With each repeat survey, space photography becomes less expensive whereas aerial photo costs remain constant

Geography. *This Gemini view east over the Nile Delta to the Suez Canal, Red Sea, and Dead Sea was taken at an altitude of close to 115 miles and provides a broad perspective of a portion of the world's surface which currently and for thousands of years has been the focus of man's attention*

lite will carry three television cameras. One, sensitive to the blue-green part of the spectrum, will give a good look at underwater features. The second, in the near infrared, is best for looking at vegetation. The third will provide additional pictures for other color combinations. The photographs could be used for a variety of purposes: determine the distribution and vigor of vegetation, measure the movement of glaciers, measure the effluents of rivers, monitor the levels of lakes and reservoirs and the growth of deltas, and assess air and water pollution. From these data, USGS will be able to construct small-scale thematic or topical maps on such things as land use and vegetation.

The satellite may carry a small telecommunications unit to relay data to and from ground station. "Getting data from remote locations can be a problem," according to Fischer. "Sending a man out to read an instrument is expensive. So is building long transmission lines. Besides being less expensive, sending a signal up to a satellite gives us information almost instantaneously. The information provides a basis for action and is not just something for the his-

torical record," he points out. Among the possibilities Fischer is considering for the data-relay package: tiltmeters on volcanoes, strain gages in a geological fault, and gages for measuring stream levels.

Future possibilities

USGS is now conducting research on a number of more sophisticated remote sensors for possible use in future satellites. Some of this research is aimed at developing new instruments specifically for resource observation purposes; other research is evaluating instruments developed elsewhere in the government, principally the military. Using these instruments for aerial sensing, USGS has lined up a number of interesting future prospects:

• Scanners for detecting infrared energy emitted from the earth. Essentially, this is a way of detecting differences in temperature. Preliminary research indicates that infrared imagery could be used to map geothermal power sources and to monitor and eventually predict volcano eruptions. Also, infrared imagery can be used to supply data such as those from a recent infrared survey of Hawaii

where more than 200 large, previously unknown springs were discovered issuing into the ocean from the island. The cooler spring waters appeared as darker areas on the infrared image.

• Radar imagery. The Carlin, Nev., gold mine—the largest new gold mine in the U.S.—is associated with a previously unrecognized fault structure, according to radar images. The images suggest that other nearby areas should also be explored.

• Ultraviolet light scanners. USGS believes it is possible to discover new phosphate deposits by observing their luminescence when they are stimulated by ultraviolet.

USGS summed up its hopes for the EROS program this way at a recent briefing before the Senate Interior and Insular Affairs Committee: "The resources potential of observation from space can be the subject of lengthy speculations, but in all probability some of the largest benefits will come from applications as yet undefined, and perhaps unimagined. We expect the unexpected, and we are prepared to adjust our programs to take advantage of these unforeseen uses."

Clean Air Act Cleans Up

*Selbyville, Del., is the first area to feel the muscle of
the act's pollution abatement powers. Actions are under way
in nine other areas, with more in the offing*

Selbyville, Del., say its citizens, stinks. Nauseating, sickening, obnoxious, disgusting—not to mention indescribable —have also been used to describe the town's odor since 1955 when Bishop Processing Co. set up shop two miles south of Selbyville in Bishop, Md. The company, which employs 45 people, renders chicken parts, fish, and bone meal into animal feed and fertilizer.

Selbyville should be smelling better before too long. Acting under the air pollution abatement powers of the Clean Air Act, the Department of Health, Education, and Welfare has ordered Bishop Processing to stop by Dec. 1, 1967, the "discharge of malodorous air pollutants." The action follows a public hearing, the first called under the act.

Enforcement procedure

The Clean Air Act, passed in 1963 and amended in 1965 and 1966, empowers HEW to take action to abate specific air pollution problems. On interstate pollution, HEW can act on its own or at the request of a state governor (or the state's air pollution control agency). On intrastate pollution, HEW can act only at the state's request.

The first step is a conference of the interested parties. If the conference decides that effective progress toward pollution abatement is not being made and that the health or welfare of any persons is being endangered, it recommends remedial actions. At least six months must be allowed for the actions to be carried out.

If the conference recommendations are not carried out in the allotted time, HEW can then appoint a board of five or more to hold a public hearing on the problems. If the board finds that pollution is occurring and that effective progress toward abatement is not being
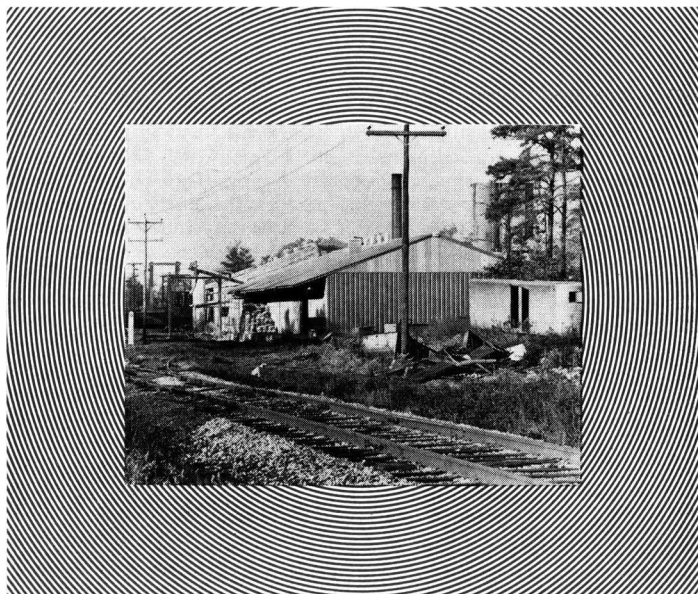
The Source. *From this small rendering plant of the Bishop Processing Co. came a variety of malodorous air pollutants that led the governor of Delaware to request action by HEW under the Clean Air Act*

made, the board recommends remedial actions. Again, at least six months is allowed for compliance. If the recommendations are not carried out, the Attorney General can bring suit on behalf of the U.S. to force compliance.

The Selbyville case was undertaken at the request of the governor of Delaware. The conference, the first to be called under the Clean Air Act, was held in Selbyville on Nov. 9–10, 1965. The description given of Selbyville is virtually the same as that given at the public hearings a year and a half later.

The odor—identified as coming solely from Bishop Processing—affects the health and welfare of the community. It causes headaches, nausea, vomiting, difficulty in breathing, choking, and irritability. Sleep is interrupted; respiratory ailments are aggravated. Laundry costs are increased—and even then the odor persists in clothing. Many homeowners installed air conditioning to make life more bearable in the summer when the odor is worse because the winds frequently are from the south. Outside activity is impossible.

The odor discouraged new industry from coming in. Tourists passing through passed through fast. Population declined. Teachers were hard to recruit. Just living in Selbyville came to be an embarrassment. The chief of police told of going to police conventions and being greeted with "Here comes Stinky."

Selbyville and Delaware officials indicated they had exhausted every available voluntary, persuasive, and legal recourse before invoking the Clean Air Act. Maryland officials said that state and local laws could not deal with the problem (the legislation has been strengthened since).

The conference concluded that Selbyville's pollution was subject to abatement under the Clean Air Act and recommended that Bishop Processing immediately institute a vigorous clean-up program, to be followed by routine good housekeeping and sanitation. The company was given until Sept. 1, 1966, to institute its overall control program.

Hearing called

The public hearing was set for May 17, 1967, following reports from the states of Delaware and Maryland indicating that Bishop Processing had not taken adequate control action. After two days of testimony, the public hearing board agreed that, although Bishop Processing had made some effort to control the pollution, effective progress was not being made. The board also found that "effective, feasible, and reasonable measures" were available.

During the testimony, government witnesses said that a $40,000 expenditure would control dryers, cookers, and tallow tanks, and thus stop the discharge of pollutants. Company president Howard Polin said that the company had already spent that much on control measures. One of the results was that Maryland then claimed that the plant's air pollution devices were polluting the streams.

Polin also complained that he hadn't been able to get clear recommendations from state and federal authorities. "We're like a man who's been asked to walk down the road and when he asks where he's going, he's told, 'Just keep going, we'll tell you when you get there,'" he said. "If we're hesitant, it's because we don't seem to have accomplished anything with what we've done. Today is the first time we have heard any specific program that we should follow. If we knew that in doing this and spending the money we wouldn't have this harassment and these problems, we'd do it," Polin told the board.

Polin is getting his wish, for the board's recommendations are highly specific. Bishop Processing was directed to:

• Vent offal rotary dryer to an afterburner operating at 1200° F. with a minimum residence time of 0.3 second.

• Discontinue the processing of chicken skins in the bone dryer.

• Vent feather-meal dryer to potassium permanganate scrubber.

Air pollution abatement actions taken under Clean Air Act

Area: Selbyville, Del.–Bishop, Md.
(Bishop Processing Co.)[a]
Initiated by: Delaware governor
Status: Hearing board recommendations issued May 1967. Compliance required within six months

Area: Shoreham, Vt.-Ticonderoga, N.Y.
(International Paper Co.)[a]
Initiated by: Vermont governor
Status: Conference held December 1965. Recommendations being implemented as per schedule; completion set for June 1968

Area: Garrison, Mont.
(Rocky Mountain Phosphates Co.)[a]
Initiated by: Montana governor
Status: Only intrastate action. Conference to be held August 1967

Area: Lewiston, Idaho-Clarkston, Wash.
(Potlatch Forests, Inc.)[a]
Initiated by: HEW
Status: Conference held March 1967. Recommendations call for creation of interstate control agency; control of refuse disposal; company action to control odors by end of 1967

Area: Interstate Washington, D.C., metropolitan area
Initiated by: President and HEW
Status: Conference not yet scheduled. Field and laboratory tests under way; completion set for end of 1967

[a] Single pollution source indicated.

Area: New York-New Jersey metropolitan area
Initiated by: New York governor and HEW
Status: Conference held January 1967. Recommendations call for creation of interstate control agency, control of sulfur oxide emissions from combustion of sulfur-bearing fuels, emissions of sulfur compounds from industrial processes, carbon industrial emissions, and emissions from Abex Corp., Mahwah, N.J.

Area: Kansas City, Kan.–Kansas City, Mo., metropolitan area
Initiated by: HEW
Status: Conference held January 1967. Recommendations call for creation of interstate control agency; control of refuse disposal, salvage operations, and industrial process emissions; prevention of air pollution at Mid-Continent International Airport, Platte County, Mo.

Area: Parkersburg, W. Va.–Marietta, Ohio, area
Initiated by: HEW
Status: Conference held March 1967. Recommendations call for creation of interstate control agency; control of refuse disposal, salvage operations, power plant emissions, and industrial process emissions

Area: Steubenville, Ohio–Weirton and Wheeling, W. Va., area
Initiated by: HEW
Status: Conference not yet scheduled

Area: Ironton, Ohio–Ashland, Ky.–Huntington, W. Va., area
Initiated by: HEW
Status: Conference not yet scheduled

• Vent all gases from cookers through knock-out traps to surface condensers to afterburners.

• Enclose all tallow tanks and provide for ventilation of gases through a condenser to an afterburner and provide for draining condensed liquids to waste water treatment facilities.

• Treat waste water to eliminate odors by substantially separating solids and grease before oxidizing volatile organics with chlorine or by other means.

• Construct an adequately sized concrete parking and unloading pad, curbed and drained to waste water treatment facility, and resurface existing concrete apron.

• Provide a secondary fired incinerator to dispose of putrefiable solids removed from liquid wastes and other processes.

• Continue to improve general housekeeping practices and institute daily cleansing of all surfaces where putrefiable materials can accumulate.

These measures must be taken within six months, the minimum time set by the Clean Air Act.

Chairman of the public hearing board was Louis J. Fuller of the Los Angeles Air Pollution Control District. Other members: James B. Coulter, Maryland State Department of Health; Floyd I. Hudson, Delaware State Board of Health; Robert G. Yeck, Agriculture Department; and Leon S. Pocinki, Commerce Department.

Other cases

The Selbyville case is one of 10 currently being processed under the Clean Air Act. In Selbyville and three other areas, the pollution is attributed to a sole source. In the other six, the pollution is more generalized and typical of metropolitan areas. HEW foresees more cases of the latter type, since there are about 70 interstate metropolitan areas. HEW is now gathering data on these areas and expects to start proceedings shortly on a number of new cases.

HEW is pleased with progress to date in the proceedings. Except for Selbyville, the proceedings have led to abatement action that probably would not have otherwise taken place. Implementing the recommendations of the conferences and public hearings falls on the shoulders of local and state authorities, and they appear to be responding.

QUOTE . . .

STRATEGIC FORESIGHTING

Augury has made significant advances in recent times. The divination process has been greatly enhanced by the advent of systems analysis, projection models, and those magic boxes, the computers. With such modern aids, signs, symptoms, and portents can be more conveniently exhorted to cast the shadows of coming events.

In addition to augurs, oracles, and prophets there is a fourth class of practitioners, the seers, who at least deserve a hearing. I refer to the . . . people with insight who visualize situations of the future and give counsel regarding plans and appropriate action so that the risk of being caught unprepared can be reduced. When the threats of ignorance and technological change are at large in the land, it is prudent for an enterprise, public or private, to have a good seer.

Strategic planning is the specialized branch of the planning activity which is concerned with anticipating events and shaping appropriate courses of action, especially those like research and engineering, that must be initiated *in time* for an organization to be in the best position, ready and capable, to respond effectively to the threats of change and to contingencies.

Let us take [a situation] that is fraught with future uncertainty—I refer to the issue of energy supply over the next 20 or 30 years. There appears to be no serious problem wih regard to the total supply; it has been forecast to be adequate to meet the total demand. The problems arise from the competitive "mix" of the different energy-producing materials and forces like hydropower. Let us examine our energy policy from the standpoint of one of the sources, namely, bituminous coal.

Coal's share of the total energy production in the U. S. slipped from about 70% in 1900 to 23% in 1965. It lost the transportation market to oil and now faces the prospect of losing its *growth share* of the electric utility market to nuclear power and eventually the prospect of obsolescence. Besides this competitive threat, coal now must conform to stringent air pollution regulations to reduce the amount of sulfur oxides emitted by burning into the atmosphere of our largest cities. In the time-frame we are considering, up to 30 years ahead, the natural gas and domestic oil reserves are expected to decrease. These points illustrate some of the uncertainty with which a strategic foresighter must cope. The purpose [of his activities] is not to predict in the usual sense, but to discover contingent boundary conditions. Each . . . contingent need provides an opportunity for generating new ideas to overcome the technical barriers. Then the necessary research resources may be programmed to achieve the desired technical events. Thus, the approach of the strategic foresighter is to examine future potential situations, and diagnose the needs as the basis for deciding what courses of action must be initiated.

The strategic foresighter . . . takes an active part in the managerial process by helping to shape the course of action, usually by bending it in the desired direction by fostering the development of the needed technology to meet objectives.

CHARLES M. MOTTLEY

U. S. Bureau of Mines, Washington, D. C., at a discussion of forecasting techniques at Industrial Management Center conference on "Technological Forecasting for Industry," May 22–25, 1967.

Waste Management and Environmental Aspects of Nuclear Power

Joseph A. Lieberman and Walter G. Belter

Division of Reactor Development and Technology, Atomic Energy Commission, Washington, D. C. 20025

The growth of competitive nuclear power in the U. S. and greatly increased public interest in the quality of our environment make it timely to examine the waste management and environmental aspects of nuclear electric power generation. During the past two years there have been more discussions and deliberations on clean water, clean air, waste management, and restoring the quality of our environment by scientists, engineers, technical administrators, and many congressional groups, than in any previous period of our nation's development.

In general, the results of these assessments and more than 20 years of operating experience show that radioactive waste management operations are being carried out in a safe and economical manner, without harmful effect on the American public, environment, or resources. With this experience and with the reactor technology now being developed, the nuclear industry might well contribute to the reduction of current environmental pollution problems, particularly atmospheric pollution.

Contamination from nuclear energy operations is different in certain important respects from nonnuclear pollution—it cannot be detected by the human senses, it can cause damage to human tissues, and, in certain instances, it has a long effective life. Thus, new techniques have been required for its management. Although the basic principles of radioactive effluent control and environmental and public health protection in the nuclear industry are similar to those which apply to other chemical or heavy industries, there is one significant difference between this industry and others. From its inception, the nuclear industry was acutely aware of the potential hazardous effects of its wastes and focused detailed attention on these problems.

As a result, probably greater scientific and technical effort has been brought to bear on radioactive waste problems and perhaps more money has been spent, on a comparable basis, to control the effluents of this industry, than on any other industrial waste.

Preventive approach

The industry's activities and operations in this area have been strongly characterized by a "preventive" approach rather than a "curative" one. This does not imply that all problems in this area have been completely solved; however, satisfactory waste management systems have been field tested on an engineering scale, and advanced reactor technology and fuel reprocessing technology are now being developed to provide the base for continued control.

Despite extensive discussions and published information on this subject, "radioactive wastes" continue to be considered by most people as a single uncategorized entity. The layman considers waste from nuclear reactors, from laboratory research, from medical use, or from chemical reprocessing of irradiated fuel elements, as one and the same thing. The specialist, however, recognizes certain fundamental factors which must be considered in the evaluation of any radioactive effluent control system:

• The specific nature (physical, chemical, and radiometric), quantity, and origin of the radioactive waste material being disposed.

• The characteristics (physical, chemical, and biological) of the receiving environment.

• Basic radiation protection standards or criteria.

Origin and nature of radioactive wastes

Effluents of widely varying character in terms of volume, concentration, and chemical makeup originate in the various

FEATURE
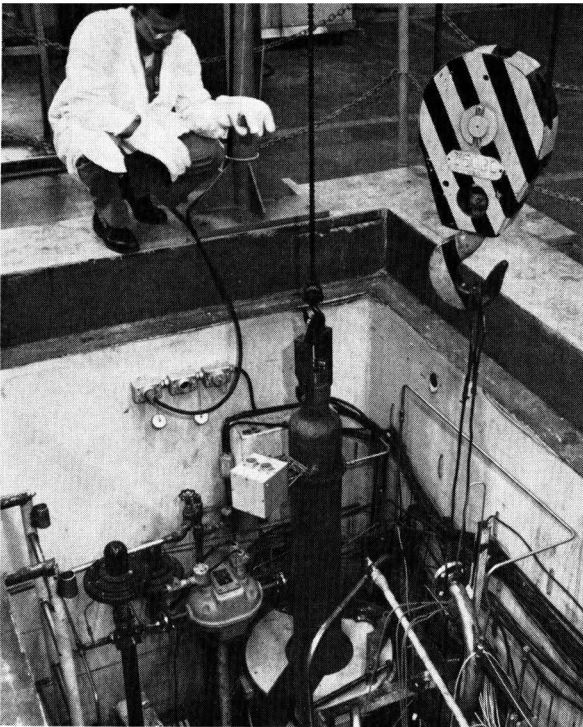
High-level wastes. *Among the promising methods for disposal of high-activity wastes from reprocessing of fuels are the continuous phosphate glass process, the radiant spray process, and the pot calcination process. Here, a technician removes a pot containing simulated high-level waste solids from a calcination furnace during research studies*

parts of the nuclear fuel cycle. In addition, the uses of radioisotopes in medicine, agriculture, and industry also generate waste materials. Because of the increasing interest in waste management from an expanding nuclear power industry, we will focus on the latter portions of the nuclear fuel cycle:

• The effluents from power reactors.
• Radiochemical processing plants, which are required for reprocessing irradiated reactor fuel for recovery of unburned uranium and plutonium.

Liquid effluents from a normal operating power reactor generally contain radioactive concentrations (mostly induced activity in corrosion products) on the order of fractions of a microcurie per liter. On the other hand, first cycle wastes from the reprocessing of irradiated nuclear fuels have concentrations of radioactive material hundreds of millions of times higher than those contained in power reactor wastes. This difference alone explains why these wastes create entirely different problems.

Most workers in the field use low level, intermediate level, and high level to characterize in a general way the categories of radioactive wastes. On the basis of the single factor of gross activity concentration, we will consider those waste concentrations greater than

a millicurie per liter to fall in the high level waste category; the microcurie to millicurie per liter in the intermediate category; and lower concentrations in the low-level category. Many workers consider only first cycle fuel reprocessing wastes in the high-level category, with all other wastes from laboratory research and power reactor operations considered low-level.

Approaches to radioactive effluent control

Waste management in atomic energy operations must control radiation hazards not only during operations but also after the waste products are discharged to the environment. Three basic approaches to radioactive effluent control have been applied successfully:

Dilute and disperse has been used only with low-hazard potential wastes, in which the radioactivity can be reduced to acceptable levels (either directly or following treatment), by dilution in nature—air or water. In the past 15 years, quantitative physical, chemical, and biological data have been obtained on such things as dispersion phenomena and reconcentration factors, demonstrating the validity of this approach without compromising health and safety standards. While this pro-

cedure has permitted safe development of the nuclear energy industry within the Atomic Energy Commission complex, it has not been used to date in power reactor effluent control operations.

Concentrate and contain is used for high-activity liquid waste originating from chemical processing of irradiated reactor fuel. The radioactivity is concentrated by volume reduction and is then confined or isolated in a controlled area such as specially designed underground storage tanks, away from man and his natural resources. Containment is essential for high-activity wastes because small volumes would require excessive amounts of environmental dilution.

Delay and decay has been used to discharge certain kinds of liquid wastes to the ground at suitable locations. Soil holdup or exchange capacity is used in this concept. Either direct discharge to the environment or discharge after conventional treatment may be involved.

In establishing engineering or operational criteria for satisfactory waste management systems, detailed quantitative consideration must be given to:

• The specific nature and quantity of radioactive wastes being handled.

• The characteristics of the receiving environment.

• The interaction between the two.

• The basic radiation protection guides or standards, as established by the Federal Radiation Council (FRC) or the National Council on Radiation Protection and Measurements (NCRP).

Radiation protection criteria

The basic radiation protection standard is the radiation dose to man. National and international scientific advisory bodies have promulgated maximum permissible dose standards. Secondary standards, termed maximum permissible concentrations (MPC), have also been established to enable the translation of the basic "dose" standards to operating criteria or standards. The basis of these MPC's is that a continuous lifetime exposure to these levels will not deliver a radiation dose sufficient to produce detectable biological damage.

FRC and NCRP in the U. S. and the International Commission on Radiological Protection (ICRP) indicate that such results may be averaged over a one-year period. FRC, NCRP, and ICRP have recommended that the annual dose to an individual residing in the vicinity of a controlled area should not exceed $1/10$ of the basic radiation dose standard for occupational exposure. Consequently, the applicable MPC must be reduced by a factor of 10. NCRP and ICRP have not recommended specific values of MPC for the population at large, but ICRP has suggested that, for planning purposes, a reduction factor of 100 be used where genetic exposure is involved and a reduction factor of 30 be used where somatic exposure is involved.

Dilute and disperse

In the "dilute and disperse" approach, radiation standards may be applied at either the "point of discharge" or the "point of exposure." From a regulatory standpoint, it appears simpler to devise engineering standards of a quantitative specification type for the "point of discharge." But more than 15 years of experience and operating data on dispersion phenomena and reconcentration factors have shown that it is reasonable, under proper circumstances, to utilize the environment for receiving

Electric utility generating capacity
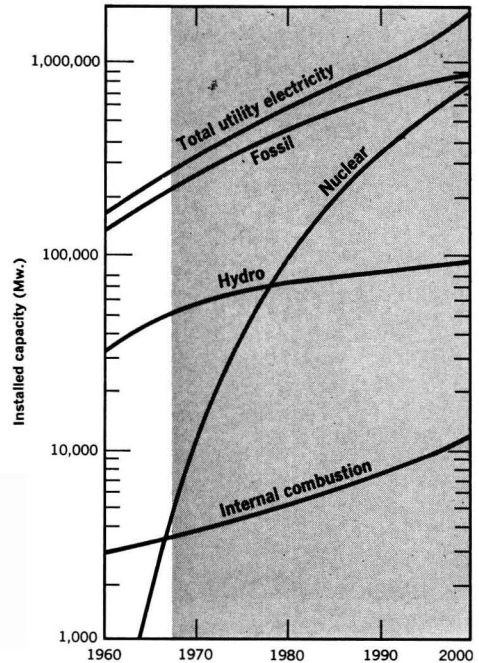
certain high-volume, low-activity waste material without compromising accepted health and safety standards.

However, the "point of exposure" approach should be used only when a detailed assessment of all environmental conditions, including geohydrology and meteorology, is available on a continuous basis. Furthermore, the approach requires continued evaluation of the effects of radioactive decay, dilution, and the reconcentration of radionuclides in our ecological system. Safe utilization of environmental dilution capacity is applicable only for certain environments and those types of wastes generally characterized as large-volume, low-activity waste. High-activity waste, resulting from the chemical processing of irradiated reactor fuel, will probably require complete containment.

From both a technical and administrative standpoint, radiation protection standards should be used as guides. The regulatory function should be that of assuring adequate performance and establishing operational criteria. Competent technical analysis, interpretation, and judgment are obvious requisites in discharging the regulatory function. In the formulation of such criteria, three basic principles should apply:

• The minimum practicable amount

of radioactive materials should be dispersed into the environment. The determination of "practicable amounts" can only be made by a quantitative assessment of specific environments and situations to assure protection of the public health and safety and by the characteristics (treatment requirements) of specific wastes.

• Continuing or periodic monitoring is mandatory to assure that established criteria are being followed and radiation protection standards or guides are being met.

• Performance criteria must be modified as required by changes in environments, operating situations, or waste materials.

The potential effluent control problem from nuclear power systems may be considered in two parts—(1) the handling, treatment, and disposal of increasing quantities of liquid, solid, and gaseous wastes with very low levels of radioactivity from the normal operation of civilian nuclear power stations, and (2) the processing and disposal of much smaller volumes of highly radioactive wastes from commercial processing facilities, which result from the processing of irradiated reactor fuel to recover unburned fissionable material.

Nuclear Power Reactors

The management of radioactive waste is not expected to impede the development of large-scale and widespread nuclear power stations. However, the quantities of low-activity wastes (liquids, solids, and gases) produced require safe, effective, and economical collection, handling, and management systems. Otherwise effluent control can become the limiting operational system in a plant's power production.

The scope and magnitude of these operations vary with each type of power reactor. For example, the satisfactory handling and disposal of gaseous effluents is an important design consideration for organic, gas-cooled, and direct-cycle, boiling-water reactors. Water-type reactors, the predominant type in the U. S., produce significant quantities of low-activity liquid wastes, which are either treated prior to disposal or are reused as reactor feed water. For the longer term, the nature and quantity of low-activity wastes from thermal and liquid metal fast breeder reactors will be evaluated as part of the overall development of these reactor systems.

Waste systems for power reactors have been constructed, based on conservative design criteria in terms of safety, pollution control, and plant performance. These criteria include the following salient features:

• Plant capacities are sized to handle abnormal volumes and activities caused by higher than expected corrosion and leakage rates, frequency of maintenance, and radioactivity from fuel failures.

• Plant flexibility is provided to accommodate waste from future fuel types, new decontamination solutions, and unforeseen abnormal wastes and cleanup solutions from accidents.

• Some dilution of liquid wastes, by mixing with main condenser discharge water or other water, is permitted in order to remain well below radiation protection standards; however, the dilution capacity of surface water streams receiving the condenser discharge water is not used to meet the standards.

• Limited use is made of on-site disposal for low- and intermediate-level liquid wastes or packaged, solid wastes.

• Piping and tanks (for all except very low-activity liquids) are placed in pipe trenches and in concrete enclosures so that leakage can be collected and returned to the waste system.

Burying. *Solidified high-level radioactive wastes can be stored in abandoned salt mines. The wastes are trucked to the mines, lowered by cable to a carrier in the mine, and then carried to the capped hole in the mine floor. As part of the test, one bay is provided with heaters to determine if heat has any deleterious effects on the mine pillars*

Surface waste carrier
Hoist and work platform

Nonradioactive array
Pillar heaters
Fuel assembly array
Waste disposal carrier
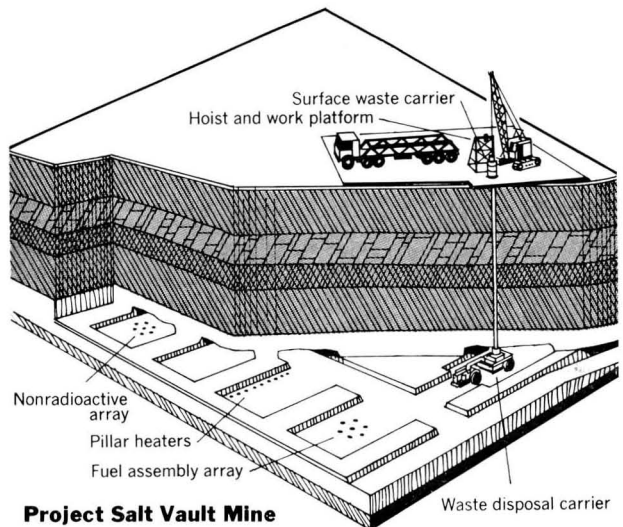
Project Salt Vault Mine

Grout injections. *One technique for solidification of radioactive wastes is the hydrofracturing process. A slurry or grout of cement, diatomaceous earth, and waste is forced into suitably oriented fractures in impermeable shale formations. The prototype (right) is a hydraulic fracturing plant; the cross section (opposite page) is a schematic of a fracturing plant and the injected grout sheets*
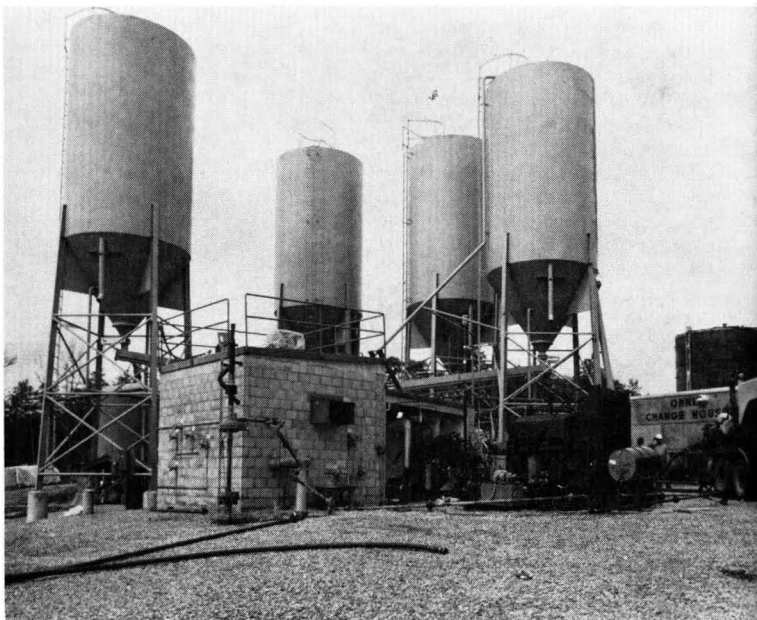
Treatment and storage systems at the presently operating water reactors (those planned for the expanding industry in the next decade or more) include decay holdup tanks, evaporators, ion exchangers, steam-stripping, catalytic recombination of hydrogen and oxygen, fixation of solids and liquids in concrete, incineration, baling, and liquid and gas filtration.

Liquid wastes

In many cases, liquid wastes are processed by decay storage and monitoring prior to release, without any other treatment. The waste volumes handled at power reactor facilities to date are not large (2000 to 45,000 gallons per day for 50 to 270 Mw$_e$. reactors) in comparison with industrial waste volumes from many other industries.

The total radioactivity handled in these wastes is also quite small (ranging from less than 1 to 10 curies per year, mostly activated corrosion products such as cobalt-58, chromium-51, manganese-54, iron-59, and molybdenum-99). Radioactivity concentrations in existing power plant liquid effluents, with no environmental dilution, have ranged from 1 to 5% of internationally accepted radiation protection standards. In most cases, the plants have not taken

credit for identification of the specific radionuclides present, which is a further factor of conservatism used.

Solid wastes

Solid waste volumes for water reactor plants amount to several thousand cubic feet per year. These low-level solid wastes are disposed of through commercial land burial operations at special locations in New York, Kentucky, Nevada, and Washington. The availability of suitable land burial facilities does not appear to be a problem for future power reactor operations.

Solid combustible wastes are generally baled by standard baling machines; volumes are reduced by a factor of about five. The bales are sealed in fiber drums or boxes and shipped to the burial sites. Ion exchange resins, evaporator concentrates, and contaminated noncombustible waste are fixed in concrete in standard 55-gallon drums and transported by commercial firms to the burial sites.

Gaseous wastes

Radioactive gases (nitrogen-13, argon-41, krypton-85, and various isotopes of xenon—133, 135, and 138) are normally produced in water-cooled and

moderated reactors through radiolytic decomposition and irradiation of reactor water, impurities, and any traces of air in the water. Defects in fuel element cladding also permit fractions of the fission gases present in the fuel to be released in the reactor coolant water.

Some of the radioactive effluents may be associated with particulate matter. All potentially contaminated air and gas streams discharged to the atmosphere pass through high efficiency absolute filters which remove 99.9% of the particles 0.3 micron or larger. Some plants have holdup capacities for up to 30 days to permit radioactive gases to decay and discharge under favorable atmospheric conditions.

Radioactive gaseous effluents from nuclear power plants are continuously monitored; further off-site monitoring is also provided by state and federal agencies. Environmental monitoring data indicate that there has been no detectable increase in atmospheric radioactivity from nuclear power plants. Nuclear power plant records indicate gaseous discharges that are 0.1% of permissible limits.

Cost data

Capital costs for waste management for present water-type reactors (50-270

Hydraulic fracturing plant

Dry solids storage bins
Injection well
Gray shale
Limestone
Grout sheet
Red shale
Grout sheet

Cased observation well

Depth (feet)
20
200
400
600
800
1,000
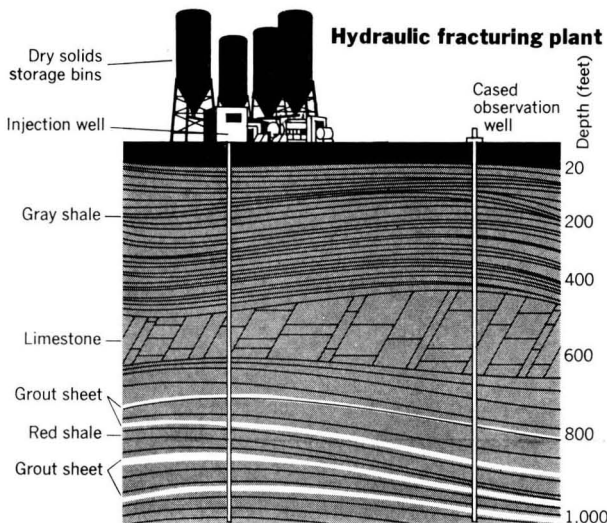
waste accumulated by 1980 would reach 36 million gallons.

The intervening years have brought improvements in fuels technology and in fuel reprocessing methods which have served to reduce markedly the volume of high-activity reprocessing wastes generated per unit of nuclear power produced. Thus, while estimates of installed nuclear power in the year 2000 remain approximately the same as previously projected, those in 1980 have risen by a factor of four—from 25,000 Mw_e. at the time of the hearings to the present 95,000 Mw_e. forecast; but predicted accumulated waste volume in storage by 1980 has dropped by a factor of 15—from 36 million gallons to 2.4 million gallons. Even with the currently projected nuclear power growth rate, the cumulative waste volumes by the year 2000 are estimated at about 40 million gallons; to date AEC has satisfactorily handled 65 million gallons of high activity wastes.

Storage as liquids

These estimates assume that the wastes will be stored as liquids for long terms in tanks. More than 20 years' experience with storage of liquid high-activity wastes in tanks has shown it to be a safe, practical means of interim handling, but the long-term usefulness of this method is possibly limited. Accordingly, AEC has pursued a vigorous research and development program aimed at developing and demonstrating, on an engineering scale, systems for conversion of high-level liquid wastes to stable solids, with subsequent long-term storage or disposal in a dry geologic formation such as salt.

Storage as solids

With adoption of a conversion-to-solids waste management concept, approximately 1 cubic foot of solid waste would be produced per 100 gallons of high-activity waste. Preliminary engineering and economic evaluations indicate a 30-year interim storage of waste solids before final disposal; by the year 2000, the rate of production of waste solids will require about 1.2 acres of salt mine space per year.

This solidification and disposal technology for high-activity waste has reached the hot engineering-scale plant and field demonstration phase. In December 1963 the Waste Calcining

Mw_e.) have ranged from $0.5 to $4.0 million for the collection, processing, disposal, and monitoring systems required. Capital costs for such facilities presently constitute 3–5% of total reactor cost; waste system operating and maintenance costs have ranged between 5 and 10% of the overall plant operation and maintenance costs. Present engineering estimates for new light water power reactors in the 500–1000 Mw_e. range, include waste systems costs of about 1 to 1.5% of the total capital investment.

Thermal pollution

From an overall water pollution standpoint, a significant problem in the future may be thermal pollution from both nuclear- and fossil-fueled electric power plants. The magnitude and severity of thermal pollution problems depend largely on local environmental conditions. The availability of adequate surface water supplies for condenser cooling is becoming a major consideration in selecting sites for both nuclear and conventional thermal-electric generating stations.

Because of a lower thermal efficiency, nuclear plants of current design discharge more waste heat to the environment than a conventionally fired plant

of the same size. This disparity will likely be reduced with improved plant performance of advanced reactors now under development.

Auxiliary cooling systems, involving reservoirs, ponds, or cooling towers, can be a solution, but installation costs of $7 to $10 per kilowatt of plant capacity may be required over a conventional river water cooling system. However, these costs may be offset by increased flexibility in site selection, which could result in lower costs for fuel, power transmission, and land.

Fuel Reprocessing Plants

During chemical reprocessing of irradiated reactor fuel to recover unburned uranium and plutonium, highly radioactive wastes are produced which must be contained and isolated from man and his natural resources for literally hundreds of years. The magnitude of the high-activity waste management problem with an expanding nuclear power industry has been under continuing assessment as an integral part of the AEC's radioactive effluent control R & D program. For example, during hearings in 1959, the Joint Committee on Atomic Energy was told that, using the then current processing technology, the volume of high- and intermediate-level

Waste solidification engineering prototypes

Solidification. *Three processes for waste solidification—spray solidification, pot solidification, and continuous glass phosphate solidification—seem particularly promising, and have been demonstrated in prototype operations.* Spray solidification *involves spraying liquid waste through an atomizing nozzle into the top of a heated cylindrical tower; as it falls, the atomized waste is evaporated, dried, and calcined to a powder. The powder is melted (temperatures from 700° to 1200° C.), then channeled into a receiver where it is solidified for storage. The* pot solidification *process involves heating liquid wastes in a pot placed in a multiple-zone furnace. The wastes first pass through a thick sludge-like state, then (at about 900° C.) are converted to calcine. The pot then is cooled and sealed for storage. In the* continuous phosphate glass process, *liquid waste is mixed with phosphoric acid, then concentrated in an evaporator. The resulting thick slurry is fed into a continuous melter where final evaporation and glass formation occur at 1000° to 1300° C. The molten glass flows into a receiver and is solidified for storage. The diagram (above) shows the flow for the* prototype systems. *The two main flow paths show the waste solidification process for the three alternate systems and the auxiliary equipment involved. The picture (right) shows one of the process plug-in equipment racks with acid fctraionator and waste evaporator vessels*
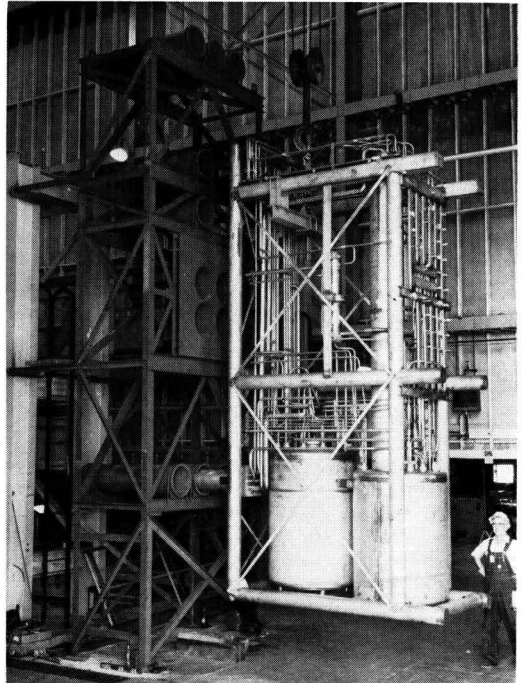
Facility at the National Reactor Testing Station became the world's first plant-scale facility for converting actual high-level radioactive wastes to a safer, solid form. The plant was satisfactorily operated for about one year. It was then shut down for approximately $1\frac{1}{2}$ years while additional solids storage bins were constructed; it is now back in operation.

The technology for solidification of high-level waste from power reactor fuel reprocessing has also reached the engineering-scale demonstration phase; a plant at the AEC's Hanford plant near Richland, Wash., went "hot" in late 1966.

Extensive laboratory and field research by Oak Ridge on the storage of high-level waste solids in a salt mine culminated in a full-scale field test at the Carey Salt Co. mine in Lyons, Kans., which started in November 1965. In-place measurements of the radiation and thermal effects on the structural stability of salt are continuing. Industry is receiving the results as commercial reprocessing of spent reactor fuel goes operational during the 1966–72 period.

Chemical reprocessing

Intimately related to progress in high-level waste solidification are substantial improvements in chemical reprocessing. These improvements have reduced the volumes of waste and the nonradioactive dissolved solids in the wastes. High-level waste volumes ranging from 1000–1500 gallons/ton U processed have been reduced to tens of gallons/ton U during the past six to seven years. This attack on the problem at its source represents an important contribution in the waste field.

Recovery of fission products

The panacea for all industrial waste problems—the recovery and beneficial use of waste by-products—has frequently been suggested as a solution to the nuclear energy waste disposal problem. Similar suggestions have been made that waste management costs might be markedly reduced by recovery of fission products from the waste. While the idea is attractive, fission product recovery operations have not substantiated this enthusiasm. In general, a fission product yield of 90% is satisfactory for by-product use, but for waste disposal purposes, decontamination factors of 10^6 to 10^8 are required before the effluent could be satisfactorily discharged to the environment.

Oak Ridge studied the effects of fission product removal, using optimistic expectations of waste compositions from future fission product separation processes. This study indicated that fission product recovery did not provide any significant economic advantage for waste management. The cost of managing wastes that are 90 to 99% depleted in fission products is about 70% as much as the cost of managing wastes with no fission products removed. The difference, about $400 per metric ton of uranium processed, does not pay for separation and handling of fission product concentrates. The problem and costs of disposing of the fission product radiation sources after they have served their purpose as radiation devices would still remain. Therefore, removal of fission products should be justified and paid for by the market for fission product radiation or heat sources. From an environmental or overall waste management standpoint, fission product *recovery* cannot be equated to fission product *removal*.

Cost data

The costs of high-activity waste treatment and ultimate storage in the nuclear power future have been estimated between 0.02–0.03 mill per kwh. of nuclear electricity produced. This represents about 1–2% of the total fuel cycle cost and substantially less than 1% of the cost of nuclear power in a 4 mill per kwh. economy. Based on laboratory and engineering process data, and on an expected successful field demonstration and testing program with high-activity waste, waste management costs probably will not deter the development of safe and economical nuclear power—even with the latest power projections.

Rare gases

The presently proposed waste management systems will fulfill the requirements for safe and economical disposal of high-level wastes from our future nuclear power industry; still, two potential long-range problems require additional attention. These involve the release of increased quantities of krypton-85 and tritium to the environment.

Although the rare gases are less hazardous than many other fission products, the release of krypton-85 at fuel reprocessing plants located near populous areas may impose certain operational limitations. An expanding nuclear economy may require removal and containment of krypton-85 to prevent a significant buildup of this radionuclide in the atmosphere. Technology to accomplish this is being developed in AEC's waste research program.

Tritium, a fission product of very low yield, may also merit special consideration from the standpoint of its management in wastes from fuel processing. In the case of present solvent extraction plants, at least 75% of the tritium in the irradiated fuel is discharged to the environment in low-level aqueous wastes. Future plants in less remote locations may be restricted in the quantity they can release to their immediate environs.

Environmental Studies

AEC has carried out a wide variety of environmental studies (stream and river, estuary and oceanographic, soil and earth) to provide specific information on the fate and behavior of low-level effluents dispersed in specific environments. In this manner, AEC can assess more accurately and specifically the environmental effects of waste disposal practices and establish rational technical criteria for safe dispersal of radioactive effluents to the environment.

Clinch River study

A prime example of the environmental studies carried out in the AEC waste disposal program was the comprehensive stream investigation on the Clinch and Tennessee Rivers below the Oak Ridge National Laboratory. This study involved various federal and state agencies and scientific disciplines; it was successful because of the close cooperation and active participation of each group. Participating in the study were the Tennessee Valley Authority, AEC, Geological Survey, Public Health Service, Tennessee Department of Public Health, Tennessee Game and Fish Commission, and Oak Ridge National Laboratory.

Normal monitoring practices at Oak Ridge had determined that the concentration of radioactivity in the Clinch and Tennessee Rivers below Oak Ridge

Solidification and salt mine disposal seem most promising for high-activity wastes

	1970	Calendar Year 1980	2000
Installed nuclear capacity (Mw$_e$.)	11,000	95,000	734,000
Volume high-level liquid waste[a,b]			
Annual production (gal./yr.)	23,000	510,000	3,400,000
Accumulated volume (gal.)[c]	45,000	2,400,000	39,000,000
Accumulated fission products (megacuries)			
Sr-90	15	750	10,800
Kr-85	1.2	90	1,160
H-3	0.04	3	36
Total fission products	1,200	44,000	860,000
Solid waste production (ft.^{3}/yr.)[d]	230	5,100	34,000
30-yr. interim solid storage			
Volume in storage (ft.^{3})	450	24,000	390,000
Length 48-ft.-wide canals (ft.)	5	265	4,300
Disposal in salt mines			
Area required (acres/yr.)	0	0	1.2
Accumulated area used (acres)	0	0	1.7

[a] Based on 100 gal. high-level acid waste per 10,000 Mwd(th) irradiation.
[b] Assumes 3-yr. lag between dates of power generation and waste production.
[c] Assuming wastes all accumulated as liquids.
[d] In a conversion-to-solids concept, 1 cu. ft. of solid waste is produced for each 100 gal. of high-level waste. Assuming a 30-year interim storage of solids, by the year 2000, the rate of production of waste solids would require about 1.2 acres of salt mine space per year.

was well within internationally acceptable standards; still, further fundamental and applied information was needed on the physical, chemical, and biological dynamics of a flowing fresh water system receiving low-level radioactive wastes.

The ultimate fate and distribution of radionuclides of specific interest at Oak Ridge—strontium-90, cesium-137, ruthenium-106, and cobalt-60—were extensively studied through field and laboratory work from January 1960 to December 1964. Continuous proportional water sampling showed that more than 90% of the strontium-90 remained in the dissolved phase in the reach between Oak Ridge National Laboratory and Chattanooga, as did 79–94% of the ruthenium-106 and 70–98% of cobalt-60; only 8–31% of the cesium-137 remained.

Further demonstration that cesium-137 becomes rapidly and permanently associated with suspended sediments was the fact that radioactivity *versus* depth profiles of bottom cores from contin-

J. A. Lieberman

Dr. Joseph A. Lieberman *is Assistant Director for Nuclear Safety, Division of Reactor Development and Technology, AEC, a position he has held since 1961. Dr. Lieberman joined the AEC's Division of Engineering in 1949, and was appointed chief of the Environmental and Sanitary Engineering Branch in 1956. Previously (1946–49), he was engaged in hydrologic research with the Forest Service, following military service with the Corps of Engineers in the Pacific area in World War II. He received his Bachelor of Engineering degree (1938) and Doctor of Engineering degree (1941) from Johns Hopkins University. Dr. Lieberman is secretary of the Subcommittee on Waste Disposal and Dispersal of NAS, chairman of the Waste Disposal Subcommittee of the American Standards Association, and a member of the Interim Committee on Nuclear Wastes of the Federation of Sewage and Industrial Wastes Association, the Subcommittee on Radioactive Waste Disposal by Incineration of the National Committee on Radiation Protection, the Committee on Water Resources Research of the* Federal Council for Science and Technology, Sigma Xi, *and a Diplomate of the American Academy of Sanitary Engineers.*

W. G. Belter

Mr. Walter G. Belter *is chief of the Environmental and Sanitary Engineering Branch of the AEC's Division of Reactor Development and Technology, a position he has held since 1961. Mr. Belter joined the Division in 1957. Prior to 1957 he was associated with the Indiana State Department of Health and the Air Force in positions involving the design, construction, and operation of domestic and industrial waste treatment facilities, including the design of the radioactive waste handling system at Wright-Patterson AFB, Ohio (1955–57). Mr. Belter received his B.S. (1949) and his M.S. (1950) in civil engineering from the University of Wisconsin. He holds a professional engineering degree from the state of Indiana. He is a member of the American Nuclear Society, WPCF, Confederation of Federal Sanitary Engineers, American Society for Civil Engineers, and Conference on Radiological Health.*

uous sedimentation zones showed a marked correlation with annual cesium releases from the laboratory. Of the total radioactivity released to the river by the laboratory during its 20-year history (corrected for decay), 21% of the cesium-137, 9% of the cobalt-60, 0.4% of the ruthenium-106, and 0.2% of the strontium-90 became associated with the bottom sediments in the first 21 miles below the laboratory.

Based on sediment cores, only a relatively small quantity of radioactivity has accumulated in the bottom sediments—approximately 200 curies or about 1.5% of the total radioactivity released to the river since 1944. Results of desorption tests indicate that radionuclides in the sediment would not be released by leaching with river water.

Biologically speaking, the study indicates that an insignificant amount of the total radioactivity discharged is held in the biomass at any given time, even under the most conservative estimates relative to biota production and uptake. For example, based on the maximum concentration of strontium-90 observed in fish and the known phosphate concentration in the river, a maximum total strontium-90 load of 30 millicuries in the biomass was calculated for the Clinch River embayment of Watts Bar Reservoir (10^9 cubic feet). Therefore, for a relatively clean stream such as the Clinch River, the amount of radioactivity stored in the bottom sediments and biomass was very small. The potential hazard from any accidental release of activity from a "built-up reservoir" within the river system is, indeed, negligible.

Model stream studies

Comprehensive field stream studies will not be possible, however, on all major water courses where nuclear facilities will be built. Therefore, the University of Texas is studying a 200-foot long model stream which can be controlled hydraulically and biologically to simulate various stream environments. Results of the study show that stream biomass can be important as a temporary radionuclide reservoir in the type of sluggish, weed infested (highly productive) stream common in certain areas in summer.

The studies also show that the photosynthesis to respiration (P/R) ratio gives an immediate indication of whether or not biological uptake or release is occurring. An increase in the suspended sediment load of a stream will "rob" radionuclides from the biomass because the radiochemical equilibrium changes. This study is continuing, with emphasis on development of mathematical models and on an analysis of the parameters of multiuse streams receiving other types of waste effluents in addition to radioactivity. Steady and unsteady radioactive discharges are being studied to develop a universal transport model. Such models would be useful in calculating consequences of both continuous and possible accidental radioactive releases to the environment.

CBI studies

The Chesapeake Bay Institute (CBI) of Johns Hopkins University, and others, have carried out for AEC field, empirical, and theoretical studies of physical dispersion of radioactive effluents in estuarine and coastal waters. A comprehensive study of New York Harbor, involving field measurement of currents, temperature, and salinity by the Coast and Geodetic Survey and data analyses by CBI, has provided a means for evaluating the safety of nuclear ship operations within the harbor.

The CBI work is now emphasizing development of improved methods for predicting distribution of excess temperature resulting from discharge of power plant condenser cooling water into the marine and estuarine environment. In a search for an economical method to obtain rapid initial mixing of heated effluents with receiving waters, CBI is also studying the discharge of these effluents as a horizontal jet having large initial momentum compared to that of the receiving waters.

In field studies involving introduction of a tracer dye into the heated discharge, the spatial distributions of both dye concentration and temperature are being determined. This will verify the predicting technique, as well as the validity of assumptions made regarding mixing of the effluent with the receiving waters and the rate of heat loss to the atmosphere.

Conclusions

Restoring and maintaining the quality of our environment are rapidly becoming important national objectives. This was reiterated in late 1966 at the National Air Pollution Conference at which the problems of pollution from automobile exhaust, sulfur dioxide, carbon dioxide, and oxides of nitrogen were discussed in great detail. Several speakers noted that nuclear energy is a "clean" source of power and that it should play a significant role in eliminating these sources of environmental pollution.

Five to six years of waste management experience at large water-type reactors have shown that power reactor effluent control can be carried out in a safe and economical manner, without harmful effects on the public, its environment, or natural resources. Waste processing technology and environmental science have been and are being developed which will continue to provide satisfactory pollution control systems for the expanding nuclear power industry. In addition, we believe that this "clean" source of energy can, with safety and economy, make a significant contribution to reducing our nation's overall environmental pollution problem.

Selected additional reading

Belter, W. G., "U. S. Operational Experience in Radioactive Waste Management (1958–1963)," in third International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, Aug. 31 to Sept. 9, 1964.

Blanco, R. E., et al, "Future Magnitude and Proposed Solutions of the Waste Disposal Problem," in Proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, Feb. 14–18, 1966, CONF-660208.

Blomeke, J. O., "Waste Management Economics in a Future Atomic Energy Industry," in annual meeting of the National Technical Task Committee on Industrial Wastes, St. Louis, Mo., Dec. 11–13, 1963.

Culler, F. L., "Nature of Radioactive Wastes," Joint Committee on Atomic Energy Hearings on Industrial Radioactive Waste Disposal, volume 1, 32–57, Jan. 28, 1959.

Final Report on the Clinch River Study, Oak Ridge, Tenn., 1967, ORNL—4035.

Industry Woos Public with Pollution Prevention Line

(Anncr, voice over) You might say this story is for the birds! **(Music in and under) (Anncr, voice over)**...or even a bit of a fish story! Avery Island, Louisiana. A sanctuary for rare heron, egret and ibis. Here also in these scenic surroundings, Humble Oil & Refining Company produces thousands of barrels of oil. Yet hardly a feather is ruffled because Humble takes extra care to keep the area close to its original natural state. **(Music up and under)** As for the fish. You'll see fish like these downstream from Humble's Baytown refinery. Humble spends millions of dollars each year to help keep nature undisturbed, to preserve fishing grounds, and to conserve the natural resources we
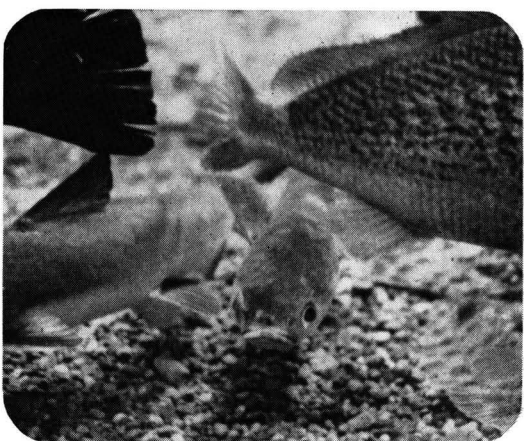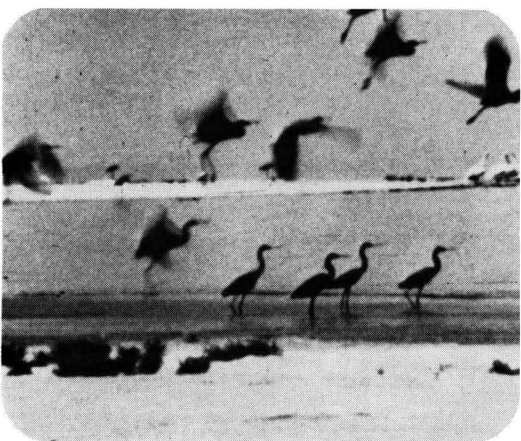
TV commercial takes positive approach,

tells viewers what company has done

to prevent pollution at its Louisiana refinery

use. That's the kind of company we are. If that's the kind of company you'd like to do business with, here's the place to do it. Stop in and fill up with High-energy Enco/Esso Extra Gasoline. Let the Tiger Team put a Tiger in your tank. Happy motoring. **(Music up and out)**
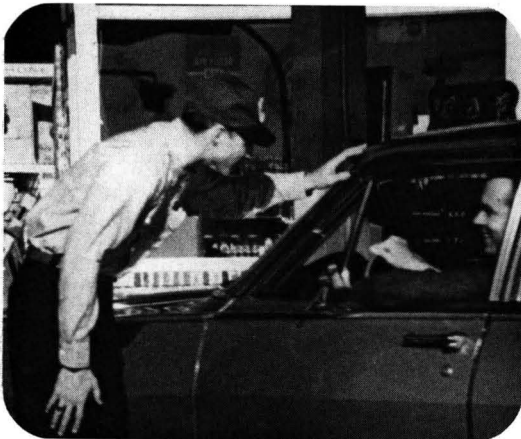
"We believe that industry should respond to the desires of society rather than react to the threat of regulation," Mr. H. H. Merideth said recently (April, 1967) at the annual meeting of the National Petroleum and Refiners Association. "Industry must provide major leadership in air conservation, not because it is necessarily the greatest culprit, but because of its amassed technical skills and its economic understanding which is so necessary to feasible solutions," he continued. Mr. Merideth is coordinator of air and water conservation for the Humble Oil and Refining Co.

Last year Humble Oil was awarded the Izaak Walton League of America's Honor Roll Award for "foresighted leadership" in water conservation. In presenting the award, Mr. Reynolds T. Harnsberger, national president of the league, cited the company's Baytown, Tex., refinery for its three-lagoon, 380-acre water purification system.

The company is one of many industries which have waged public and private campaigns for pollution abatement—pamphlets on clean air and water, films, speeches before university and community groups, and advertising efforts.

Humble decided to tell the story of its positive actions in helping to maintain a wholesome environment. The still photographs and commentary here are from a one-minute television commercial being shown around the nation.

Evaluation of Gas Chromatographic Columns for Analysis of Subparts per Million Concentrations of Gaseous Sulfur Compounds

Robert K. Koppe and Donald F. Adams

College of Engineering Research Division, Washington State University, Pullman, Wash.

■ A bromine coulometric microtitration cell was used to measure the loss of sulfur-containing gases on empty gas chromatographic columns constructed of various materials. Stainless steel was the most satisfactory material tested. Sulfur-compound losses were then determined on stainless steel columns packed with solid support materials and stationary phase liquids in various combinations. Porapak Q was tried as a gas-solid partitioning material. Detection limits for three sulfur compounds on a 10% Triton X-305 Chromosorb G DMCS-treated and a Porapak Q column are reported. Losses on the column require that sulfur compounds in the ambient air within the usual concentration range be concentrated 10- to 50-fold before separation on currently available columns.

The quantitative and qualitative determinations of the various sulfur-containing gases in the ambient air have been impeded by a lack of convenient, specific, and sensitive analytical procedures.

Typical compounds include hydrogen sulfide, sulfur dioxide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. The quantity of each of these gases varies greatly with the type of sources present within different communities.

Studies of the concentrations of sulfur compounds using conventional wet chemical methods have shown that the concentrations in the atmosphere are generally below 1 p.p.m. and range downward to concentrations below the threshold of human sensory detection (Adams and Koppe, 1966; U. S. Department of Health, Education, and Welfare, 1964). In the case of hydrogen sulfide and methyl mercaptan, this is in the 1- to 10-p.p.b. range (Young and Adams, 1966).

Numerous complicated analytical schemes have been devised for the sampling and analysis of these gas mixtures. Conventional wet chemical methods involve a different analysis procedure or separate sampling technique for each major compound type mentioned. Furthermore, chemical techniques cannot distinguish among the various possible mercaptans or organic sulfides which may be present in a given sample.

Gas chromatography overcomes the inherent weaknesses of wet chemical techniques and provides a separative tool, which in association with a detector of suitable sensitivity and specificity could provide a detailed analysis of the sulfur-containing compounds in the ambient air. Recent advances in gas chromatographic detector technology have provided sensors with improved sensitivity and sulfur compound specificity.

A 1963 evaluation in our laboratory of commercially available sulfur-specific gas chromatographic detectors showed that the Dohrmann iodine microcoulometric cell provided the best over-all sensitivity for the various sulfur compounds found in pulp mill emissions (Adams, Koppe, et al., 1965). Other microcoulometric cells, such as the silver–silver sulfide detector, have been used to determine hydrogen sulfide and mercaptans (Fredericks and Harlow, 1964). However, the applicability of this detector for analysis of the broad spectrum of sulfur compounds is limited by its inadequate response to sulfur dioxide or alkyl sulfides and disulfides.

A bromine coulometric microtitration cell with improved sensitivity and stability has been developed in this laboratory (Adams, Jensen, et al., 1966). The sensitivity is in the range of 5 to 50 p.p.b. for typical sulfur compounds found in some industrial areas. For example, an injection of a 10-ml. volume of 25-p.p.b. hydrogen sulfide or methyl mercaptan through a rubber septum in a glass T-tube installed in the system immediately upstream from the titration cell produced a recorder response twice that of the base line noise. Normal carrier gas and supplemental gas flows were maintained during these tests. Unfortunately, duplicate samples injected onto a chromatographic column did not produce any recorder response on the same detector. Ten- to 250-fold increases in sample concentrations were required for detection in the column effluents. This paper reports the influence of column materials and packing upon the losses of sulfur compounds when passed through the chromatographic column.

Experimental

Instrumentation. A Beckman ThermotraC column oven was used isothermally at 25° and 70° C. or programmed over various temperature spans. A Dohrmann microcoulometer Model C-200 with certain modifications was combined with the improved bromine microcoulometric detector (Adams, Jensen, et al., 1966; Bureau, Koppe, et al., 1967). The chromatograms were recorded on a Leeds & Northrup Model H, 1-mv. full-scale recorder operating at a chart speed of $^1/_2$ inch per minute. Helium carrier gas flow was in the range of 50 to 170 ml. per minute and was augmented with up to 120 ml. per minute of helium at the column outlet to provide the necessary flow for the microtitration cell. A flow of 170 ml. per minute was originally established as the optimum flow to the microtitration cell, but recent work indicates that 100 ml. per minute afford increased sensitivity with no increase in noise level. Stainless steel columns of $^3/_{16}$-inch outside diameter were used throughout the studies of column packings.

Preparation of Standard Gas Samples. Standard gas concentrations were prepared in flexible containers made from a Mylar-Dacron laminate (Schjeldahl Co., Northfield, Minn., Type X-308) by heat-sealing the edges of the plastic laminate with a thermosensitive Mylar film (Schjeldahl Type GT-400). Standard gas concentrations prepared in our laboratory have been held in these containers for 24 hours with no change in concentration.

Ten-, 50-, and 100-liter bags were used. Hydrogen sulfide, sulfur dioxide, and methyl mercaptan were obtained from pressure cylinders (Matheson Co. and Dow Chemical Co.) and injected into the bags with Hamilton gas-tight syringes. Dimethyl sulfide and dimethyl disulfide (Eastman Kodak), liquids at room temperature, were injected into the bags using Hamilton microsyringes. A glass marble, placed in the bag during fabrication, was used as a surface on which the dimethyl sulfide and dimethyl disulfide were spread. The

bag was then heated with a heat gun to speed vaporization of the sample. The relative standard deviation for preparation of gas mixtures in this manner is $\pm 9.5\%$ (Adams, Jensen, et al., 1966).

Column Packing. Column packings were prepared by dissolving the stationary phase in a suitable solvent in a large evaporating dish. The column packing material was then added and the evaporating dish placed on a steam bath where the material was gently stirred while the solvent evaporated. A stream of dry nitrogen directed over the evaporating dish aided in the final drying. The evaporating dish was then placed in a drying oven at 70° to 80° C. for several hours to complete the removal of solvent.

In one experiment, 1% phosphoric acid was added to Chromosorb G and Aeropak 30 before coating with stationary phase. This had been suggested as one way to prevent loss of the acid sulfur gases on the column packing. The acid was diluted with water, the packing material was added, and the water was removed on a rotating evaporator which was heated with a water bath. The stationary phase was then added by the procedure outlined above. Addition of phosphoric acid did not enhance the recovery of sulfur gases from the columns.

Column packing material was placed in the column either by gravity with light tapping to aid in packing or by use of Pres-Pak which uses compressed gas to move the packing. Selection of method depended on the type of material being packed. Granulated fluorocarbons tend to stick or ball up and therefore were packed by the gravity method.

Extensive evaluations of partition liquids and gas-solid columns have been reported (Adams and Koppe, 1958, 1959). Several of the partition liquids which had previously been noted to give good peak separation were re-evaluated during the course of this study with respect to their use with the very low levels of pollutant gases. Table I lists solid support materials which have been tried. Table II lists partition liquids used in earlier studies.

Porapak Q and silica gel were also evaluated as gas-solid partitioning materials.

Small-diameter coated capillary columns were not tried because the maximum sample which could be injected in this type of column was less than one tenth of that which is possible in the packed column, and more supplemental gas would have to be added to the very low carrier gas flow to provide the flow required by the microtitration cell. This would further dilute the eluted components and eliminate any advantage over the packed columns.

Of all the partition liquids and solid supports tried, only Triton X-305 on Chromosorb G and Porapak Q as a gas-solid column were selected for further study. They provided the best observed sample recovery, the maximum ability to separate sulfur gas mixtures which included sulfur dioxide, and the most satisfactory peak conformation. Column conditions are presented in Table III.

Results

Losses on the column tubing were first determined with various empty columns mounted in the column oven. A glass T-tube with rubber septum was installed in the system immediately upstream from the titration cell to permit direct sample injection into the cell. The response of the cell to direct injection was compared to the response obtained for equal volumes of sample injected into the column. The re-

Table I. Solid Support Materials

Chromosorb P	Gas-Pack F
Chromosorb G	Aeropak 30
Chromosorb W	Anakrom
Fluoropak 80	Gas-Chrom RZ
Fluoroport T	Gas-Chrom Q
Teflon 6	Porapak Q

Table II. Partition Liquids

Cenco Hyvac oil	Tergitol N-27
Paraffin	Siliclad
DC 550 silicone oil	Lanolin
DC 550 silicone oil and	
stearic acid (10%)	Apiezon M grease
Quadrol	Polyglycol P-1200
Pluronic L-61	TCP
Flexol TOF	Triton X-15
Carbitol	Triton X-35
Squalane	Triton X-45
Di-*n*-butyl phthalate	Triton X-100
Di-*n*-octyl phthalate	Triton X-102
β,β'-Iminodipropionitrile	Triton X-114
Dinonyl phthalate	Triton X-165
Polyethylene glycol 6000	Triton X-205
Benzyl Cellosolve	Triton X-305
Dimethyl phthalate	

Table III. Column Conditions

	10% Triton Chromosorb G–DMCS	Porapak Q
Length, feet	8	6
Diameter, inch	$^3/_{16}$	$^3/_{16}$
Carrier gas flow, ml./min.	50	170
Make-up gas flow, ml./min.	50	0
Initial temperature, ° C.	30	60
Time at initial temperature, min.	4	0
Final temperature, ° C.	70	140
Time for elution of dimethyl disulfide, min.	15	17

Table IV. Recovery through Empty Tubing

	Compound					
	H_2S		CH_3SH		SO_2	
	Column Temperature, °C.					
	25	70	25	70	25	70
	Column Material					
Glass, %	87	39	92	75	56	69
Stainless steel, %	101	61	99	120	52	50
Teflon, %	91	105	107	122	53	81

Table V. Detectable Concentrations by Direct Injection and through Columns

	Direct	10% Triton–Chromosorb G–DMCS	Porapak Q
H_2S, p.p.m.	0.025	0.25	0.20
CH_3SH, p.p.m.	0.025	0.25	0.20
SO_2, p.p.m.	0.100	25.0	Undeterminable

covery of three compounds at two temperatures from three types of column material is given in Table IV.

In addition, H_2S was injected into aluminum columns, but none was recovered. Therefore, no further studies were made with aluminum tubing.

All subsequent evaluations of sulfur compound losses on the column packing were made using stainless steel tubing. The detectable concentrations of three sulfur compounds by direct injection into the detector and through the gas chromatographic column are compared in Table V.

A report on the use of Porapak Q for the separation of mixtures of sulfur-containing gases indicated that good peak shapes and separations had been obtained (Aerograph Research Notes, 1966). These conclusions were confirmed for all compounds studied except sulfur dioxide. Two different lots of Porapak Q did not provide sharp sulfur dioxide peaks. On the contrary, the peak was unsatisfactory, low, and broad, making it impossible to determine a sulfur dioxide detection threshold.

Discussion and Conclusions

The loss of sulfur compounds experienced on conventional, gas-liquid or gas-solid columns is too large to permit direct determination of typical concentrations of sulfur compounds in the ambient air. In the absence of sulfur dioxide, Porapak Q provided excellent compound separation and a gain of approximately 20% in the recovery of the sample from the column packing. If sulfur dioxide is present in the sample, a 10% Triton X-305 gas-liquid column is preferable because of its ability to separate sulfur dioxide from methyl mercaptan to obtain a gas chromatographic analysis of typical atmospheric concentrations (Figure 1).

Although highly sensitive and sulfur-specific gas chromatographic detectors are now available, it will undoubtedly be necessary to concentrate the sulfur compounds approximately 10- to 50-fold. Such concentration might be accomplished by adsorption (Adams, Koppe, *et al.*, 1960), absorption (Cave, 1963), or freeze-out (Bellar, Brown, *et al.*, 1963) sampling techniques. The application of these techniques will
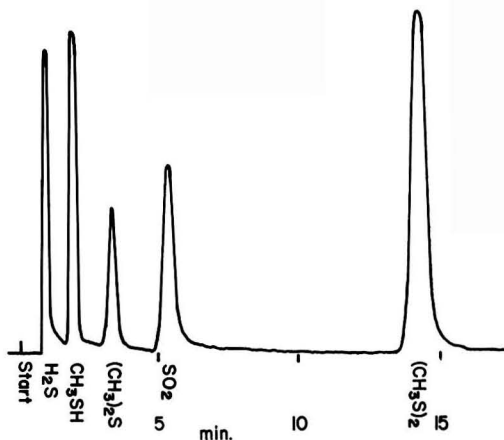

Figure 1. Five-component sulfur gas sample

Column. 8-foot × $^3/_{16}$-inch o.d. stainless steel
Solid support. Chromosorb G, DMSC-treated, 60-80 mesh
Stationary phase. 10% Triton X-305
Carrier gas flow. 50 ml. per minute
Column temperature. 30° C. for 4 minutes and then programmed to 70° C. in 6 minutes

require careful standardization because of the differences in column loss for each different sulfur-containing gas.

Alternative possibilities for direct analysis of atmospheric samples in the parts per billion concentration range include discovery of new column packings with significantly reduced affinity for sulfur compounds or the development of highly selective prefilters to be used with the microtitration cell.

Literature Cited

Adams, D. F., Jensen, G. A., Koppe, R. K., Steadman, J. P., Robertson, T. J., *Anal. Chem.* **38**, 1094–6 (1966).
Adams, D. F., Koppe, R. K., *Air Pollution Control Assoc. J.* **16**, 314–16 (1966).
Adams, D. F., Koppe, R. K., *Tappi* **41**, 366–72 (1958).
Adams, D. F., Koppe, R. K., *Tappi* **42**, 601–5 (1959).
Adams, D. F., Koppe, R. K., Jungroth, D. M., *Tappi* **43**, 602–8 (1960).
Adams, D. F., Koppe, R. K., Tuttle, W. N., *Air Pollution Control Assoc. J.* **15**, 31–3 (1965).
"Aerograph Research Notes," Walnut Creek, Calif., p. 7 (Spring 1966).
Bellar, T. A., Brown, M. F., Sigsby, J. E., Jr., *Anal. Chem.* **35**, 1924–7 (1963).
Bureau, R. A., Koppe, R. K., Adams, D. F., *Chemist-Analyst* **56**, 37–8 (1967).
Cave, G. C. B., *Tappi* **46**, 1–28 (1963).
Fredericks, E. M., Harlow, G. A., *Anal. Chem.* **26**, 263–6 (1964).
U. S. Dept. of Health, Education, and Welfare, Public Health Service, "Study of Air Pollution in the Interstate Region of Lewiston, Idaho, and Clarkston, Wash.," Publ. **999-AP-8** (1964).
Young, F. A., Adams, D. F., 74th Annual Meeting, American Psychological Association, New York, 1966.

Technique of Streaming Current Detection and Applications

Paul H. Cardwell

The Dow Chemical Co., Midland, Mich. 48640

■ A technique making use of a streaming current measurement is used to study the adsorption on polyethylene of dodecyl benzene sodium sulfonate and cetyl dimethyl benzyl ammonium chloride. The data obtained indicate that the charge density of the adsorbed layer on polyethylene increases with increasing concentration of dodecyl benzene sodium sulfonate and various quaternary salts up to their critical micelle concentrations. Beyond the critical micelle concentrations the charge density of the adsorbed layer remains constant over the concentration range which appears to correspond to that portion of the adsorption curve from the critical micelle concentration to the point of maximum adsorption. The adsorption of cetyl dimethyl benzyl ammonium chloride by sodium bentonite is reported using the streaming current technique. The exchange of sodium with the quaternary ion can be followed to the cationic exchange capacity of the clay as well as the adsorption of the quaternary salt by the clay beyond the cationic exchange capacity point. The adsorption isotherm for the system beyond the cationic exchange capacity point is given. Titrations of large organic ions could be performed with a fair degree of accuracy using the streaming current technique.

This paper describes a technique which is finding increasing applications in solution-solid systems that involve adsorption such as flocculation, stabilization, and coagulation. The apparatus used was a Streaming Current Detector developed by Gerdes (1966). The instrument is simple to operate, makes continuous and nearly instantaneous measurements.

A simplified diagram of the apparatus is given in Figure 1. The main part is the plastic cell body or boot containing a sample reservoir, a dead-ended bore, electrodes, and piston which reciprocates in the bore to force fluid back and forth through the annular spaces between the bore and the piston. A synchronous motor mounted directly above the cell body drives the piston and actuates a reed switch synchronous rectifier. The latter is accomplished by means of a magnetic cam on the motor drive.

The piston operates at 4 c.p.s. resulting in the generation of a 4-cycle streaming current. The reed switch is phased with the generated streaming current resulting in a d.c. output which is read on a microammeter in arbitrary units. The electronic circuit is of very low impedance with silver–silver chloride electrodes.

The principle of operation of the Streaming Current Detector is that the movement of the piston causes a streaming flow of liquid in the annular space between the bore and the piston which shears the adsorbed ionic double layer. This movement of at least a portion of the diffused double layer creates a streaming current which is detected. All of the work reported herein was done using polyethylene as the material of the boot and piston with the exception of some of the data to be discussed under titrations in which glass was used.

The requirements for a liquid system upon which this streaming current technique can be used are that charged particles be present, such as ions, molecules, or colloidal materials and that these particles be adsorbed by the surfaces of the boot and piston forming ionic double layers.

The chemicals used in this investigation were the best laboratory grade that were commercially available. No attempt was made to purify them. The experimental work was conducted at 23° C.

Experimental

Adsorption-Concentration. The change in the Streaming Current Detector readings (in arbitrary units) with change in concentration of dodecyl benzene sodium sulfonate is given in Figure 2. The technique was to flow a specific concentration of the surface active material through the instrument, no recycle, until the Streaming Current Detector reading became constant. This reading is plotted against the concentration of the dodecyl benzene sodium sulfonate. Note that the readings vary with the concentration. Similar information for cetyl dimethyl benzyl ammonium chloride has been reported by Cardwell (1966) and is reproduced here as Figure 3.

These same experiments have been repeated with aqueous solutions and with dispersions of a number of different materials such as alum, clay, starch, and polyethylenimine. All of the materials investigated to date have given streaming current readings which vary with concentration. The liquid in the reservoir had to be replaced a number of times to obtain a constant reading. The streaming current reading would approach asymptotically the constant value.

The curves of Figures 2 and 3 indicate that the streaming current technique can be used for the determination of con-
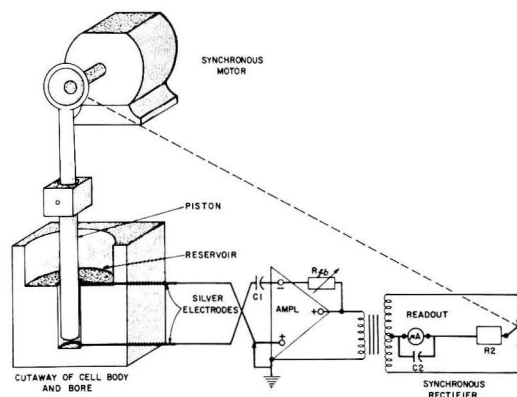

Figure 1. Simplified diagram of the Streaming Current Detector

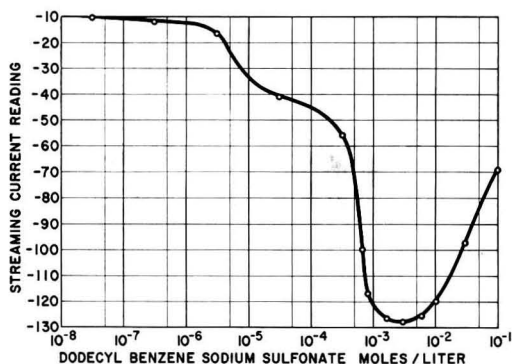*Courtesy Journal of Colloid and Interface Science*

Figure 2. Effect of concentration on streaming current reading with anionic material

Figure 3. Effect of concentration on streaming current reading using cationic material

Courtesy Journal of Colloid and Interface Science

centration. Using a calibration curve of instrument reading *vs.* concentration, an unknown concentration can be determined. Since extremely low concentrations can be detected, this is a valuable application of this technique. Figure 3 shows that the concentration of the quaternary salt could be determined to as low as 10^{-14} mole per liter. The author expects that a considerably lower concentration can be determined since the instrument reading must ultimately approach a negative 80 as weaker and weaker quaternary salt solutions are used. The negative 80 reading is that of pure water.

Experiments have been conducted which seem to indicate that colloidal particles also are adsorbed. By use of colloidal sulfur, prepared by adding a saturated normal propyl alcohol solution of sulfur to water, a negative reading is obtained. The reading is different from that given by a mixture of only normal propyl alcohol and water.

Another indication of colloid adsorption is colloidal silver iodide prepared from silver nitrate and potassium iodide solutions. Both the positive and negative silver iodides can be detected by the instrument. The positive silver iodide is prepared by using an excess of silver nitrate, while the negative sol is prepared by using an excess of potassium iodide. An interesting observation was that if the boot and piston surfaces, after being exposed to colloidal silver iodide and washed thoroughly with water, were exposed to water saturated with hydrogen sulfide, the surfaces immediately turned black because of the formation of silver sulfide on the polyethylene boot and piston surfaces.

Cleaning of the Surfaces of the Instrument. In the use of the streaming current technique, the surfaces of the boot and piston at the start of the work must be clean and free of adsorbed materials from previous work. A clean surface is one that has adsorbed upon it only water and the ions from water. Methods by which a clean surface can be obtained are by continuous washing or by exposing the liquid in the boot-piston reservoir to a new surface. In this latter technique the material on the polyethylene surfaces will desorb and be reabsorbed onto the new surface. The technique for this cleaning operation is to add activated carbon or activated silica, or both, to pure water and circulate the water through the apparatus with a screen in the circulation line to prevent the carbon and silica from contacting the boot and piston.
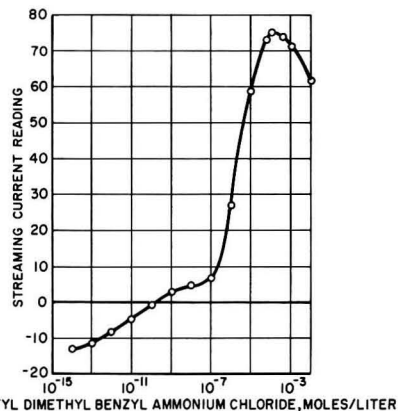
The best way to determine if the surfaces are clean is to make a measurement with pure water. In this manner, the clean surfaces do not become contaminated and a reproducible reference point for all future work is obtained.

Investigation of Adsorption by a Solid. The major applications of this streaming current technique will be to study or to control at a predetermined value, the adsorption or desorption of a material by a solid. The solid could be sewage particles, clay, paper pulp, latex, or paint pigments. The problem in work of this nature is that the measurement is made on the boot and piston surfaces of the instrument, and it becomes necessary to interpret what is happening at the surface of interest (sewage particle, clay, etc.) by what is taking place at the boot and piston surfaces.

The adsorption of cetyl dimethyl benzyl ammonium chloride by a monionic sodium bentonite has been reported (Cardwell, 1966), and the results are reproduced in Figure 4. The data in Figure 4 were obtained by adding $0.01M$ cetyl dimethyl benzyl ammonium chloride to an aqueous suspension of the sodium bentonite. The suspension was circulated through the boot and piston reservoir of the instrument until a constant reading was obtained, before the next addition of the quaternary salt was made.

The steep part of the curve occurs at, or very near, the cationic exchange capacity (cec) of the clay. From the curve this is 89 meq. per 100 grams of clay. By the standard ammonium acetate method, the cec of the sodium monoionic clay was 92 meq. per 100 grams of clay.

In this test, the streaming current technique indicated the point at which all of the sodium had been exchanged for the quaternary ion. This conclusion is further supported by the results obtained from taking samples periodically and analyzing the aqueous phase for sodium and chloride ions, and the suspended clay for carbon and nitrogen contents. The analytical results are given in Table I. The data of the first five samples in this table indicated with increasing amounts of the quaternary salt, an equivalent progressive increase in the carbon and nitrogen contents of the suspended clay as well as the sodium and chloride contents of the aqueous solutions.

Table I. Analyses of Samples of Cetyl Dimethyl Benzyl Ammonium Chloride and Sodium Bentonite

Meq. of Cetyl Dimethyl Benzyl Ammonium Chloride/G. of Clay

Sample	Amount cetyl dimethyl benzyl ammonium chloride added	Amount calculated from carbon content of clay	Amount calculated from nitrogen content of clay	Amount calculated from sodium content of aqueous soln.	Amount calculated from chloride content of aqueous soln.
1	0.056	0.056	. . .	. . .	. . .
2	0.099	0.097	0.106	0.103	0.083
3	0.544	0.526	. . .	. . .	0.530
4	0.866	0.869	. . .	0.862	0.814
5	0.890	0.890	0.864	0.890	0.852
6	1.54	1.23	1.18	0.890	. . .

Table II. Addition of Cetyl Dimethyl Benzyl Ammonium Chloride to Bentonite Clay Beyond Cationic Exchange Capacity of the Clay

Ca Amount Added, Moles/Liter	Cp Amount in Solution, Moles/Liter
4.6×10^{-6}	1.0×10^{-9}
9.2×10^{-6}	8.0×10^{-8}
1.4×10^{-5}	2.0×10^{-7}
1.8×10^{-5}	3.6×10^{-7}
2.3×10^{-5}	5.2×10^{-7}
3.2×10^{-5}	1.0×10^{-6}
4.1×10^{-5}	1.8×10^{-6}
5.0×10^{-5}	2.6×10^{-6}
7.2×10^{-5}	5.1×10^{-6}
9.5×10^{-5}	7.0×10^{-6}
1.2×10^{-4}	1.3×10^{-5}
1.8×10^{-4}	3.5×10^{-5}
2.9×10^{-4}	8.0×10^{-5}
4.0×10^{-4}	2.0×10^{-4}

Courtesy Journal of Colloid and Interface Science

Table I shows that up to the cec of the clay, all of the quaternary ion is adsorbed by the clay, and there is very little, if any, of the quaternary ion present in the aqueous solution. These results substantiate those obtained by the streaming current technique which indicated also that up to the cec all of the quaternary ion is adsorbed by the clay. Also, the cec of the clay, 0.89 meq. per gram of clay by the streaming current measurement agrees with the analytical results of sample 5 in Table I—namely, 0.85 to 0.89 meq. per gram of clay.

As the quaternary salt is added to the clay suspension up to the cec, the streaming current measurement is following the change in the charge condition of the clay as the quaternary ion replaces the sodium of the clay. Apparently, up to the point of complete replacement of the sodium, the clay particles are having an affect on the streaming current technique.

Adsorption Isotherm Calculation. It is possible to calculate the adsorption isotherm of cetyl dimethyl benzyl ammonium chloride–sodium bentonite system beyond the cec of the clay
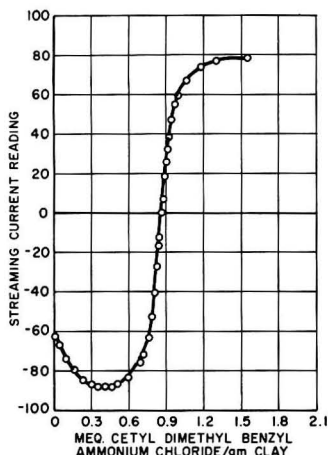

Figure 4. Addition of quaternary salt to sodium bentonite

Courtesy Journal of Colloid and Interface Science

by using the data of Figures 3 and 4. Figure 4 shows the amount (Ca) of the quaternary salt added beyond the cec. The values of Ca from Figure 4 used in these calculations are given in Table II. Using the streaming current values from Figure 4 at these concentrations, the amount actually present (Cp) in the aqueous solution is obtained by reading the corresponding concentration from Figure 3. The values of Cp corresponding to the Ca values are reported also in Table II. The difference between Ca and Cp is the amount of the quaternary salt adsorbed by the clay beyond the cec.

When the amount adsorbed by clay ($Ca - Cp$) is plotted against the equilibrium concentration, Cp, the straight line given in Figure 5 is obtained. The adsorption isotherm of Figure 5 was obtained using only data by the streaming current technique. Chemical analyses were made to check the adsorption isotherm data as measured by the streaming current technique. The point selected at which to make this comparison is that given by the last line in Table II. The streaming current technique data show that when 4.0×10^{-4} mole per liter, which is 0.65 meq. per gram of clay (from Table I,
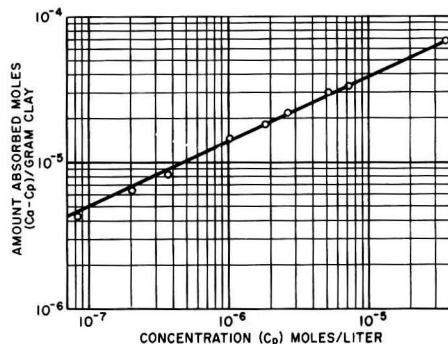

Figure 5. Adsorption isotherm—cetyl dimethyl benzyl ammonium chloride adsorbed beyond cec of clay

1.54 − 0.89), of the quaternary salt has been added beyond the cec point of the clay, half of the quaternary is in solution and half has been adsorbed by the clay. Thus, 0.33 meq. of the quaternary salt has been adsorbed per gram of clay.

The chemical analysis of this quaternary salt–clay suspension is given in Table I, sample 6. Using the carbon analysis, the amount adsorbed beyond the cec point is (1.23 − 0.89) or 0.34 meq. per gram of clay. From the nitrogen analysis, the amount adsorbed beyond the cec point is (1.18 − 0.86) or 0.32 meq. per gram of clay. Thus, the information obtained from the streaming current technique agrees with the results of the chemical analyses. Apparently, when the sodium of the clay has been replaced by the quaternary ion, the primary influencing factor on the streaming current measurement is the concentration of the quaternary ion in the solution and the amount adsorbed on the boot and piston surfaces. The clay particles seem to have very little, if any, effect on the measurement.

Charge Density of Adsorbed Layer. As the concentration of the surface active materials increases in Figures 2 and 3, the streaming current readings also numerically increase. This indicates an increase in the charge density of the adsorbed layer with concentration. There is a maximum in the curves of Figures 2 and 3, and Cardwell (1966) has pointed out that the maximum corresponds to the critical micelle concentration (cmc) of the material. The maximum or the cmc point was independent of the composition of the boot and piston when using polyethylene or glass. A detailed study of the maximum for a number of surface active materials is given in Figures 6 and 7. There is a flat top on the curves.

The work reported by Fava and Eyring (1956) for the adsorption of dodecyl benzene sodium sulfonate by cotton, had a discontinuity in the curve at 1.0×10^{-3} mole per liter. This value is the cmc for dodecyl benzene sodium sulfonate as determined by surface tension measurements. Beyond this point, the work of Fava and Eyring showed a sharp increase in the adsorption to the maximum of 3.0×10^{-3} mole per liter.

A similar adsorption curve was found by Vold and Sivaramakrishnan (1958) for sodium dodecyl sulfate by carbon. The adsorption increases regularly as the concentration of the solution increases to the cmc point. At this point, the slope of the curve increases sharply to a maximum and declines toward a limiting value. Vold and Sivaramakrishnan postulated that the rapid increase in adsorption is caused by desorption of both simple adsorbed ions and surface adsorbed micelles upon collision with micelles from the solution with the adsorbing surface in addition to the previously established processes of adsorption and desorption of single ions and adsorption of micelles.

In work with the streaming current technique (Figure 7), using dodecyl benzene sodium sulfonate, the flat part of the curve is from 1.6×10^{-3} to 3.0×10^{-3} mole per liter. This indicates there is no change in the charge density of the adsorbed layer from the cmc point to the maximum in the adsorption-concentration curve.

Titrations. An interesting application of streaming current measurements is the possibility of making titrations. To perform titrations, at least one of the materials must be adsorbed by the boot and piston surfaces and give a streaming current reading. The other material in the titration must be either of opposite charge and also adsorbed, or it must in some manner decrease the charge density of the adsorbed material on the
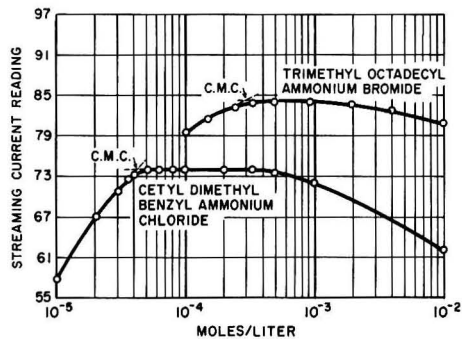

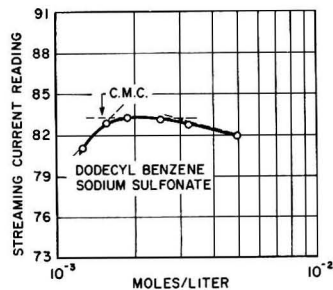Figure 6. Critical micelle concentration (cmc)

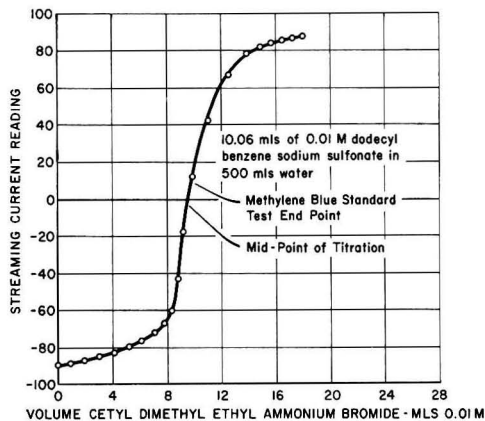Figure 7. Critical micelle concentration (cmc)

Figure 8. Titration of dodecyl benzene sodium sulfonate with cetyl dimethyl ethyl ammonium bromide

boot and piston surfaces, thus changing the streaming current reading. When the adsorption upon the boot and piston surfaces of the materials results in equal number of positive and negative charges, the instrument reads zero, and this is considered the end point.

The procedure for titrations is first to perform a preliminary one (Gerdes, 1966) to decrease any effects of a previous adsorbed film on the boot and piston surfaces and to form an

Table III. Titrations

(Dodecyl benzene sodium sulfonate used as the anion)

Cation	Concentration Anion	Concentration Cation	First Material in Instrument	Ratio Anion to Cation	Average Ratio Anion to Cation	End Point by Methylene Blue Standard Method Ratio Anion to Cation
POLYETHYLENE SYSTEM-BOOT AND PISTON						
Cetyl dimethyl ethyl ammonium bromide	0.02M	0.02M	Cation	1 to 1.03 1 to 1.03	1 to 1.03	. . .
Cetyl dimethyl ethyl ammonium bromide	0.02M	0.02M	Anion	1 to 0.99 1 to 1.03 1 to 1.00	1 to 1.01	. . .
Cetyl dimethyl ethyl ammonium bromide	0.002M	0.002M	Cation	1 to 1.05 1 to 1.00 1 to 1.00 1 to 1.05 1 to 1.03 1 to 1.01 1 to 1.01	1 to 1.02	1 to 0.98
Cetyl dimethyl ethyl ammonium bromide	0.002M	0.002M	Anion	1 to 0.97 1 to 0.97 1 to 0.985 1 to 0.90 1 to 0.95 1 to 0.90	1 to 0.95	1 to 0.98
GLASS SYSTEM-BOOT AND PISTON						
Cetyl dimethyl ethyl ammonium bromide	0.02M	0.1M	Cation	1 to 0.98 1 to 1.03	1 to 1.00	. . .
Cetyl dimethyl ethyl ammonium bromide	0.02M	0.1M	Anion	1 to 1.00 1 to 1.00	1 to 1.00	. . .
Cetyl dimethyl ethyl ammonium bromide	0.02M	0.02M	Cation	1 to 1.04 1 to 1.05 1 to 1.05	1 to 1.05	. . .
Cetyl dimethyl ethyl ammonium bromide	0.02M	0.02M	Anion	1 to 0.97 1 to 0.93 1 to 0.98	1 to 0.96	. . .
Cetyl dimethyl ethyl ammonium bromide	0.004M	0.004M	Cation	1 to 0.95 1 to 0.91 1 to 0.94 1 to 0.91	1 to 0.93	1 to 0.98
Cetyl dimethyl ethyl ammonium bromide	0.004M	0.004M	Anion	1 to 0.83 1 to 0.86 1 to 0.88	1 to 0.86	1 to 0.98
Cetyl dimethyl ethyl ammonium bromide	0.002M	0.002M	Cation	1 to 0.96 1 to 0.97	1 to 0.96	1 to 0.98
Cetyl dimethyl ethyl ammonium bromide	0.002M	0.002M	Anion	1 to 0.90 1 to 0.95 1 to 0.97	1 to 0.94	1 to 0.98
Cetyl dimethyl ethyl ammonium bromide	0.02M 0.5% KCl	0.02M 0.5% KCl	Cation	1 to 1.03 1 to 1.04	1 to 1.04	. . .
Cetyl dimethyl ethyl ammonium bromide	0.02M 0.5% KCl	0.02M 0.5% KCl	Anion	1 to 1.04 1 to 1.04	1 to 1.04	. . .

(Continued)

Table III. Titlations (*Continued*)

(Dodecyl benzene sodium sulfonate used as the anion)

Cation	Concentration		First Material in Instrument	Ratio Anion to Cation	Average Ratio Anion to Cation	End Point by Methylene Blue Standard Method Ratio Anion to Cation
	Anion	Cation				
Cetyl trimethyl ammonium bromide	0.004M	0.004M	Cation	1 to 1.02 1 to 0.90 1 to 0.92	1 to 0.95	1.0 to 1.0
Cetyl trimethyl ammonium bromide	0.004M	0.004M	Anion	1 to 0.90 1 to 0.91	1 to 0.90	1.0 to 1.0
Cetyl dimethyl benzyl ammonium chloride	0.004M	0.004M	Cation	1 to 0.94 1 to 0.91 1 to 0.92 1 to 0.99 1 to 0.99	1 to 0.95	1 to 0.99
Cetyl dimethyl benzyl ammonium chloride	0.004M	0.004M	Anion	1 to 0.89 1 to 0.90 1 to 0.87 1 to 0.90	1 to 0.89	1 to 0.99

adsorbed film which will be similar to the one obtained at the conclusion of the titration. Once this film has been formed, it should not be washed with water since this will change, by desorption, the composition of the film.

One of the simplest titrations is that given in Figure 8 of dodecyl benzene sodium sulfonate with cetyl dimethyl ethyl ammonium bromide. The curve shows that the end point, as determined by plotting the streaming current readings, agrees very well with the instrument zero end point. Using the streaming current results, the equivalent ratio between the two chemicals are 1 volume of dodecyl benzene sodium sulfonate to 0.96 volume of cetyl dimethyl ethyl ammonium bromide. A check was made using the standard methylene blue method and the ratio is 1 to 1, which agrees with the solutions as prepared of 0.01 M each.

In view of this information, various titrations using the Streaming Current Detector were made and are reported in Table III. The results of these titrations of cationic by anionic material or anionic by cationic material also do not agree with those obtained by the standard methylene blue method. The author believes that the methylene blue method gives the correct results since it agrees very closely with the compositions of the solutions as they were prepared. The results in Table III show that, compared with the methylene blue method, more anionic material usually is required for the titration by the streaming current technique regardless of the manner in which the titration is performed, anionic by cationic material or cationic by anionic material.

Apparently, in titrations, the first material to contact the boot and piston surfaces plays a very important role in the end-point determination. If the cationic material is first to contact the boot and piston surfaces less anionic material is required for the titration than if the titration is performed in the reverse manner. While a detailed study was not undertaken, part of the explanation for the results which were ob-

tained could be due to the adsorption-concentration relationship. To bring about the conditions of an equal number of positive and negative charge sites (zero reading) exposed at the shear plane of the surfaces of the boot and piston, there has to be an excess of the weaker adsorbate in the end-point solution, regardless of the manner in which the titration is performed. Thus the streaming current technique, when used for titration, appears to be in error in the direction of requiring more than the equivalent of the weaker adsorbate. Part of the explanation may also be due to the cationic material being adsorbed in a greater amount than the anionic substance, and all of the adsorbed material is not available for titration.

Conclusions

The streaming current technique can be used for following the change in the charge condition of colloidal particles in an aqueous suspension as surface active materials are being added. The technique can also be used to make adsorption studies of aqueous solutions on solid surfaces. The solid surfaces can be those of the boot and piston of the instrument or can be suspended particles in an aqueous media. While titrations can be performed, the method, because of inherent errors, results in only fair accuracy.

Literature Cited

Cardwell, P. H., *J. Colloid Interface Sci.* **22**, 430 (1966).
Fava, A., Eyring, H., *J. Phys. Chem.* **60**, 890 (1956).
Gerdes, W. F., *Instr. Soc. Am. J.* **13**, No. 12, 38 (1966).
Vold, R. D., Sivaramakrishnan, N. H., *J. Phys. Chem.* **62**, 984 (1958).

Determination of Nitrate in Estuarine Waters

Comparison of a Hydrazine Reduction and a Brucine Procedure and Modification of a Brucine Procedure

Lloyd Kahn and Francis T. Brezenski

Hudson-Champlain and Metropolitan Coastal Comprehensive Water Pollution Control Project, Federal Water Pollution Control Administration, Department of the Interior, Metuchen, N. J. 08840

■ A hydrazine reduction method and a brucine method were evaluated for the determination of nitrate in estuarine waters. The hydrazine method gave low results in many instances, which were attributed to the consumption of the available hydrazine by environmental impurities, resulting in the incomplete reduction of the nitrate to nitrite. The brucine method as described by Jenkins and Medsker was modified to give more consistent analytical calibration curves which followed the Beer-Lambert law from 0 to 0.6 mg. of nitrate nitrogen per liter. The devious behavior of the calibration curves obtained by alternative brucine procedures is explained. The precision of the recommended procedure is better than 0.03 mg. of nitrate nitrogen per liter.

The Federal Water Pollution Control Administration in determining sources of pollution of the nation's waterways and estuarine environments needs accurate measurements of chemical indicators of pollution. Many analytical methods which accurately determine chemical constituents in fresh waters are subject to interferences by the marine environment and sometimes by a particular constituent or constituents of a given estuarine environment. For example, many methods are subject to what is commonly referred to as the "salt factor" and/or are hindered by the precipitation of the calcium and magnesium hydroxides at high pH values, which are an integral part of some chemical procedures.

A useful pollution parameter is the nitrate level of a stream, as it indicates the degree of nitrification and is a part of the nitrogen cycle. Several analytical methods have been developed for determining nitrate in fresh water and sea water.

Methods

Physicochemical. These methods include the ultraviolet absorption technique of Armstrong (1963) and the polarographic method of Chow and Robinson (1953) which require more involved instrumentation and are subject to interference by humic acids and other organic compounds.

Reduction. Such techniques involve the reduction of nitrate to nitrite, which is used to diazotize an aromatic amine or phenol to produce a colored compound which is determined colorimetrically. The nitrate may be reduced to the nitrite ion either by reaction with a metal, such as cadmium, zinc, or their amalgams as was used by several investigators (Bray, 1945; Nelson, Kurtz, *et al.*, 1954; Strickland and Parsons, 1960; Chow and Johnstone, 1962; Kamphake, Hannah, *et al.*, 1967), or by use of a chemical such as hydrazine which was

used by Mullin and Riley (1955) and modified by Fishman, Skougstad, *et al.* (1964), Hikagi and Zeitlen (1962), Vaccaro, Thunberg, *et al.* (1962), and Williams and Coote (1962). These methods are subject to interferences which are peculiar to a given marine environment. For example, the Mullin and Riley salt correction factor of 0.77, although valid for the sea water used by the authors (1955), did not apply to waters around Hawaii (Higaki and Zeitlen, 1962) where a factor of 0.67 was applicable.

Direct Reaction. These techniques involve the reaction of the nitrate ion with an organic compound to yield a colored product which is determined colorimetrically. One such method is the oxidation of phenoldisulfonic acid by nitrates to give a colored compound which is determined colorimetrically (Nelson, Kurtz, *et al.*, 1954). With this method small concentrations of chloride interfere, thus limiting its use in estuarine environments.

Nitrate may react with strychnine analogs to produce colored compounds. Harvey (1960) recommends the use of strychnidine (reduced strychnine) for the "approximate" estimation of nitrate nitrogen in sea water. Fisher, Ibert, *et al.* (1958) used brucine as the reactant and found that by changing the ratio of sulfuric acid to sample volume, it was possible to determine nitrite, nitrate, or a combination of the two anions. The determination is based upon the observation that at greater than 2 to 1 ratios of water to sulfuric acid, only nitrite produces a colored compound; however, at lower than 1 to 1 ratios, the color of the nitrate reaction product predominates. In the procedure adopted as a tentative method by the American Public Health Association (1965), the nitrite interference is removed by the addition of sulfanilic acid (Boltz, 1958). Inconsistent results obtained with this procedure by Jenkins and Medsker (1964) led them to an investigation which showed that chlorides are a major source of error. This error was corrected by adding about 50 grams of NaCl per liter to both the sample and standards. They noted that the color produced for a given nitrate concentration remained constant in the presence of 27 to 50 grams of chloride ion per liter. In addition, the use of a 500 to 125 volumetric ratio of concentrated sulfuric acid to water gave more consistent results.

Because they are often used, the methods of Mullin and Riley (hydrazine reduction) and of Jenkins and Medsker (brucine) were evaluated by using water samples collected from Raritan Bay and waters tributary to Raritan Bay. A salt correction factor of 0.62 was used in the Mullin and Riley procedure. In 1963, this factor seemed to be appropriate for the determination of nitrates in the waters of Raritan Bay (Finger, 1964). However, during the present study low recoveries of known amounts of nitrate added to the water

samples were obtained. The Jenkins and Medsker brucine method gave erratic calibration curves, and a definite change in the slope of the curve was noted at low nitrate concentrations. A reversal in the order of addition of reagents and combination of the 30% NaCl and 1% brucine sulfate–0.1% sulfanilic acid solutions resulted in more repeatable calibration curves and has eliminated the change in slope often obtained near 0.1 mg. of NO_3-N per liter with the original method. The modified method is accurate to 0.02 to 0.03 mg. of NO_3-N per liter from 0.15 to 0.6 mg. of NO_3-N per liter.

Experimental

Apparatus. Spectrophotometer, Beckman Model DB, Bausch and Lomb Spectronic 20 or equivalent with 1.0-cm. cuvettes.

Water bath maintained at boiling water temperature.

Water bath maintained at 20° C.

Stock standard nitrate solution, 100 mg. of NO_3-N per liter (0.7218 gram of KNO_3 per liter of distilled water).

Standard nitrate solution, 10 mg. of NO_3-N per liter. Just prior to use, dilute 10 ml. of the stock standard nitrate solution to 100 ml. with distilled water.

Sodium chloride solution, 300 grams of sodium chloride diluted to 100 ml. with distilled water.

Sulfuric acid solution, carefully add with vigorous agitation and cooling 1 liter of concentrated sulfuric acid to 250 ml. of distilled water. Protect from moisture by keeping container capped during storage.

Brucine-sulfanilic acid reagent, dissolve 1 gram of brucine sulfate and 0.1 gram of sulfanilic acid in 70 ml. of hot distilled water. Add 3 ml. of concentrated hydrochloric acid, cool, and dilute to 100 ml. The solution should be stored in a refrigerator and is stable for several months.

Mixed reagent, just prior to use, mix 100 ml. of the brucine–sulfanilic acid reagent with 400 ml. of sodium chloride solution.
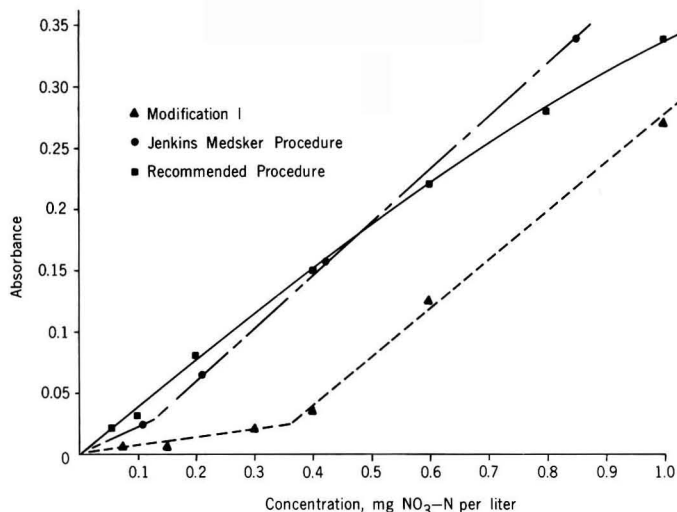

Figure 1. Nitrate results by Mullin and Riley and modified brucine procedures

Table I. Recovery of Added Nitrate Nitrogen from Various Samples

	Nitrate Nitrogen, Milligrams per Liter			
Sample No.	Original analysis	Amount added	Amount found	Recovered, %
MULLIN AND RILEY PROCEDURE[a]				
1	0.10	0.30	0.19	30
2	0.27	0.30	0.26	−3
3	0.11	0.30	0.22	37
4	0.13	0.30	0.21	24
5	0.15	0.30	0.23	27
6	0.11	0.30	0.22	33
7	0.13	0.30	0.22	30
8	0.12	0.30	0.22	33
9	0.13	0.30	0.21	23
10	0.13	0.30	0.21	23
11	0.07	0.30	0.15	27
12	0.06	0.30	0.14	27
13	0.07	0.30	0.15	27
14	0.09	0.30	0.16	23
RECOMMENDED PROCEDURE[b]				
A-1	0.08	0.10	0.18	100
A-2	0.08	0.20	0.28	100
A-3	0.08	0.40	0.48	100
A-4	0.08	0.50	0.58	100
B-1	0.15	0.10	0.25	100
B-2	0.15	0.20	0.37	110
B-3	0.15	0.40	0.55	100
C-1	0.33	0.10	0.42	90
C-2	0.33	0.20	0.52	95
C-3	0.33	0.30	0.58	83
D-1	0.38	0.10	0.46	80
D-2	0.38	0.20	0.56	90

[a] Samples 1 to 8 originated from Raritan Bay between the mouth of the Raritan River to Sandy Hook, N. J. (Chloride levels ranged from 10,000 to 16,000 mg. per liter.) Samples 9 to 14 were obtained from the Arthur Kill, Kill Van Kull, and the Narrows. (Chloride levels ranged from 12,000 to 15,000 mg. per liter.)
[b] Samples A, B, C, and D were obtained from the Raritan River at a point above the juncture of the river and Raritan Bay. (Chloride levels were approximately 12,000 mg. per liter.)

Figure 2. Representative analytical calibration curves

- ▲ Modification I
- ● Jenkins Medsker Procedure
- ■ Recommended Procedure

Absorbance (y-axis): 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.30, 0.35

Concentration, mg NO_3–N per liter (x-axis): 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0

Procedure

Jenkins and Medsker (1964) Procedure. In the absence of 2.5-cm. tubes and adaptor for the Bausch and Lomb Spectronic 20, which were specified by Jenkins and Medsker, the reactions were conducted in 20 × 200 mm. test tubes, and the measurements were made in 1-cm. cuvettes.

Into each 20 × 200 mm. test tube, pipet 10 ml. of sample, containing 0 to 0.6 mg. of NO_3-N per liter, and place in the 20° C. bath. Add 2 ml. of sodium chloride solution and mix well. Allow the contents of the tubes to come to temperature equilibrium in the 20° C. water bath. Pipet 10 ml. of sulfuric acid solution into each test tube, mix, and allow the contents of the tube to equilibrate in the 20° C. bath. Add 0.5 ml. of brucine–sulfanilic acid solution to each tube and mix thoroughly. Remove the rack of test tubes from the 20° C. water bath and place into the boiling water bath for 20 minutes. Remove the rack of test tubes from the boiling water bath and immerse them in the 20° C. bath for thermal equilibration. This prevents any further color change. Determine the absorbance at 410 mμ in a spectrophotometer using 1-cm. cuvettes.

Treat nitrate standards in the range of 0.05 to 0.6 mg. of NO_3-N per liter as described above; include standards of 0, 0.05, 0.10, 0.20, 0.40, and 0.60 mg. of NO_3-N per liter.

Recommended Procedure. To each 20 × 200 mm. test tube add 10 ml. of sample. Equilibrate in the 20° C. bath. Add 2.5 ml. of the mixed reagent and mix thoroughly. (The authors used a Vortex Jr. mixer for this purpose.) Pipet 10 ml. of the sulfuric acid solution into the test tube and mix well. Equilibrate in the 20° C. bath. Cover the test tubes with plastic caps. Place rack containing tubes in boiling water bath and heat for 20 minutes. Cool in 20° C. bath to stop color development and read absorbance against distilled water after 10 minutes at 410 mμ using 1-cm. cuvettes. Subtract blank reading from each absorbance reading to obtain the corrected absorbance. Treat nitrate standards in the range of 0 to 0.6 mg. of NO_3-N per liter as described above; include standards of 0, 0.05, 0.10, 0.20, 0.40, and 0.60 mg. of NO_3-N per liter.

Results and Discussion

Comparison of the Mullin and Riley and Jenkins and Medsker Procedures. Finger (1964) determined the nitrate content of water samples from Charleston Harbor by both the Mullin and Riley (1955) procedure and by the brucine method of Jenkins and Medsker (1964). Results ranged from 0.00 to 0.4 mg. of NO_3-N per liter by the former and 0.09 to 0.35 mg. of NO_3-N per liter by the latter procedure. This divergency in results between the methods was also found in the present study as shown in Figure 1. The data for Figure 1 were obtained on samples collected in the New York City harbor area on June 8 and August 3, 1966, respectively.

The recovery data presented in Table I indicate that the results obtained by the modified brucine procedure are more correct, therefore, some negative interference acts upon the Mullin and Riley procedure. This effect has been observed by other investigators. For example, the Mullin and Riley (1955) salt correction factor of 0.77 did not apply to ocean waters near Hawaii (Higaki and Zeitlen, 1962). Figure 1, *A*, shows that the data for the three sources of samples cluster along the same line—i.e., all nitrate values by the hydrazine method lie within the limits of 0.05 and 0.20. In Figure 1, *B*, only the nitrate results obtained on the East River samples fall within these limits, while the Hudson and Harlem River analyses more closely approach the 100% correlation line.

One contribution to the erratic results by the hydrazine method is the changing salt content of the estuarine environment. This would, of course, require applying different salt correction factors to the different samples. As all samples contained between 10,000 and 16,000 mg. of chloride per liter, the salt effect could at best account only for a small proportion of the differences.

A more probable explanation of these phenomena is indicated by the data of Kamphake, Hannah, *et al.* (1967), who show the necessity of maintaining the proper hydrazine to sample weight ratio to reduce completely the nitrate and to prevent reduction of nitrite. The authors suggest that the low nitrate recovery obtained in these samples is due to a competition of stream components for the available hydrazine,

which lowers the hydrazine level below that required for quantitative reduction of the nitrate. The relative accuracy of the two analytical methods was evaluated by the addition of known amounts of nitrate to representative samples and then assaying (Table I). The near quantitative recovery of NO_3-N by the recommended procedure is readily evident. This is in sharp contrast to the low recoveries obtained by the Mullin and Riley method.

Comparison of Recommended Procedure with the Jenkins and Medsker Procedure and Modification I. Representative analytical calibration curves obtained by the three brucine procedures are shown in Figure 2. Initial efforts to apply the Jenkins and Medsker procedure to the analysis of samples were impeded by inconsistencies in obtaining analytical curves on a day-to-day basis. These analytical curves were generally characterized by a change in slope of the Beer-Lambert law curve in the low range of nitrate concentration (Figure 2), making it difficult to distinguish small differences in concentrations at low nitrate contents. Another aspect of the problem lay in the great difference in absorbances corresponding to a given nitrate content which occurred periodically. These facts necessitated construction of a complete calibration curve with each set of determinations. The first attempt (Modification I) to reduce these adverse effects, consisted of combining the NaCl and brucine sulfate–sulfanilic acid solutions and adding the mixed reagent to the cool acidified sample solution to minimize errors in the addition of brucine sulfate–sulfanilic acid solution, which was felt to be subject to a major pipetting error. The effect of this modification is shown in Figure 2, in which the change in slope is accentuated and shifted to higher nitrate concentration.

In the recommended procedure, the mixed sample–brucine sulfate–sulfanilic acid–sodium chloride solution, was treated with the sulfuric acid causing the generation of heat during the acid addition. The analytical calibration curve obtained by this procedure is shown in Figure 2. In addition to yielding analytical calibration curves having no break in slope, the curves, although varying to some extent on a batch-to-batch basis, were much more consistent with regard to absorbance

vs. concentration. This procedure was therefore adopted for all subsequent determinations. On the basis of these data, the brucine reaction with nitrates when conducted in the cold probably differs in its reaction kinetics and stoichiometries from that obtained at elevated temperatures, causing a break in the analytical calibration curves. This conclusion is based on the break in the analytical calibration curves by the Jenkins and Medsker procedure and by Modification I of this paper and upon Arrhenius' law from which one expects a doubling of the reaction rate for each 10° C. rise in temperature. The contribution of the room temperature reaction to the total reaction would thereby be negligible and should not affect the calibration curve, contrary to experience. The linear relationship obtained for the recommended procedure can be attributed to the generation of heat during the sulfuric acid addition, which prevents the formation of the initial reaction product. A comparison of data obtained by Jenkins and Medsker and by the recommended procedure on two samples whose chloride level was approximately 12,000 mg. per liter, is presented in Table II. For one set of data, the standard deviation for both procedures was 0.016. The other set gave standard deviations of 0.020 and 0.019 for the respective procedures. The "t" test, applied to both samples showed that the means of both methods were not significantly different at the 0.02 level of significance.

Literature Cited

American Public Health Association, Inc., New York, "Standard Methods for the Examination of Water and Sewage," 11th ed., p. 198, 1965.

Armstrong, F. A. J., *Anal. Chem.* **35**, 1292–4 (1963).

Boltz, D. F., Ed., "Colorimetric Determination of Non-Metals," Interscience, New York, 1958.

Bray, R. H., *Soil Sci.* **60**, 219 (1945).

Chow, T. J., Johnstone, M. S., *Anal. Chim. Acta* **27**, 441–6 (1962).

Chow, T. J., Robinson, R. J., *J. Marine Res. Sears Found.* **12**, 1 (1953).

Finger, James H., "Nitrate Determination in Saline and Estuarine Waters: Comparison of Hydrazine Reduction and Bruce Modification Methods," Laboratory Investigation No. 3 Technical Advisory and Investigation Section, Technical Service Branch, Div. of Water Supply and Pollution Control, Robert A. Taft, Sanitary Engineer Center, Cincinnati, Ohio, October 13, 1964.

Fisher, F. L., Ibert, E. R., Beckman, H. F., *Anal. Chem.* **30**, 1972 (1958).

Fishman, M. J., Skougstad, M. W., Scarbro, G. F., Jr., *J. Am. Water Works Assoc.* **56** (5), 633–8 (1964).

Harvey, H. W., "The Chemistry and Fertility of Sea Water," 2d ed., University Press, Cambridge, 1960.

Higaki, Shiro, Zeitlen, Harry, *Limnol. Oceanog.* **7**, 103 (1962).

Jenkins, David, Medsker, L., *Anal. Chem.* **36**, 610–12 (1964).

Kamphake, L. J., Hannah, S. A., Cohen, J. M., *Water Res. Intern. J.* **1**, 205 (1967).

Mullin, J. B., Riley, J. P., *Anal. Chim. Acta* **12**, 464–80 (1955).

Nelson, J. C., Kurtz, L. T., Bray, R. H., *Anal. Chem.* **26**, 1081 (1954).

Strickland, J. D. H., Parsons, T. R., "A Manual of Sea Water Analysis," Bull. No. **125**, Fisheries Research Board of Canada, Ottawa, 1960.

Vaccaro, R., Thunberg, V. C., Ketchum, B. H., *Limnol. Oceanog.* **7**, 322 (1962).

Williams, P. M., Coote, A. R., *Limnol. Oceanog.* **7**, 258 (1962).

Table II. Results Obtained on Estuarine Samples by Jenkins and Medsker and Recommended Procedures[a]

(Nitrate nitrogen, milligrams per liter)

	Sample 1		Sample 2	
	Jenkins and Medsker	Recommended procedure	Jenkins and Medsker	Recommended procedure
	0.340	0.368	0.272	0.238
	0.336	0.348	0.250	0.250
	0.365	0.358	0.222	0.250
	0.370	0.382	0.254	0.251
	0.365	0.352	0.234	0.260
	0.336	0.346	0.254	0.266
	0.330	0.374	0.207	0.272
	0.354	0.331	0.246	0.274
	0.368	0.342	...	0.286
	...	...	...	0.300
Mean	0.352	0.356	0.242	0.265
Std. dev.	0.016	0.016	0.020	0.019
"t"	0.53		2.30	

[a] Samples 1 and 2 were obtained from the Raritan River at 5- and 25-foot depths, respectively.

Determination of Nitrate in Estuarine Waters

Automatic Determination Using a Brucine Method

Lloyd Kahn and Francis T. Brezenski

Hudson-Champlain and Metropolitan Coastal Comprehensive Water Pollution Control Project, Federal Water
Pollution Control Administration, Department of the Interior, Metuchen, N. J. 08840

■ Automation of the brucine method for nitrate determination described by Kahn and Brezenski on the Technicon AutoAnalyzer resulted in a twofold improvement of precision. The automated procedure is capable of analyzing 100 samples in 7 hours with a standard deviation of less than 0.01 mg. of nitrate nitrogen per liter.

Previous investigators (Britt, 1962; O'Brien and Fiore, 1962; Henriksen, 1965; Brewer, Chan, *et al.*, 1966; Kamphake, Hannah, *et al.*, 1967) have adapted either the Mullin and Riley (1955) or the Morris and Riley (1963) procedure for the automatic determination of nitrates by the AutoAnalyzer. The Mullin and Riley procedure is based upon the reduction of nitrates to nitrite in alkaline solution by hydrazine in the presence of a copper salt solution. The nitrite is then utilized in the diazotization of sulfanilic acid or sulfanilamide and simultaneous coupling with the N-1-naphthyl-

ethylene diamine dihydrochloride to form a colored compound which is determined colorimetrically. The Morris and Riley procedure differs from the foregoing in that a column of cadmium amalgam, cadmium, or zinc filings is substituted for the hydrazine in the reduction step. These methods, although extremely sensitive, are subject to interferences found in estuarine waters which prevent the stoichiometric reduction of nitrate to nitrite. This effect is attributed by the authors to the presence of compounds which are competing with the nitrate for the consumption of available hydrazine in the former case and tend to "poison" the reduction column in the latter procedure. Although each of the investigators appears to have solved the reduction step for his particular problem, difficulties may be encountered in applying the method to other environments.

A recently developed determination, in which brucine sulfate is reacted under very acidic conditions with nitrate and the salt effect is eliminated by the addition of sodium chloride to the sample and standards, gives precise nitrate assays in estuarine and sea water (Jenkins and Medsker, 1964). The
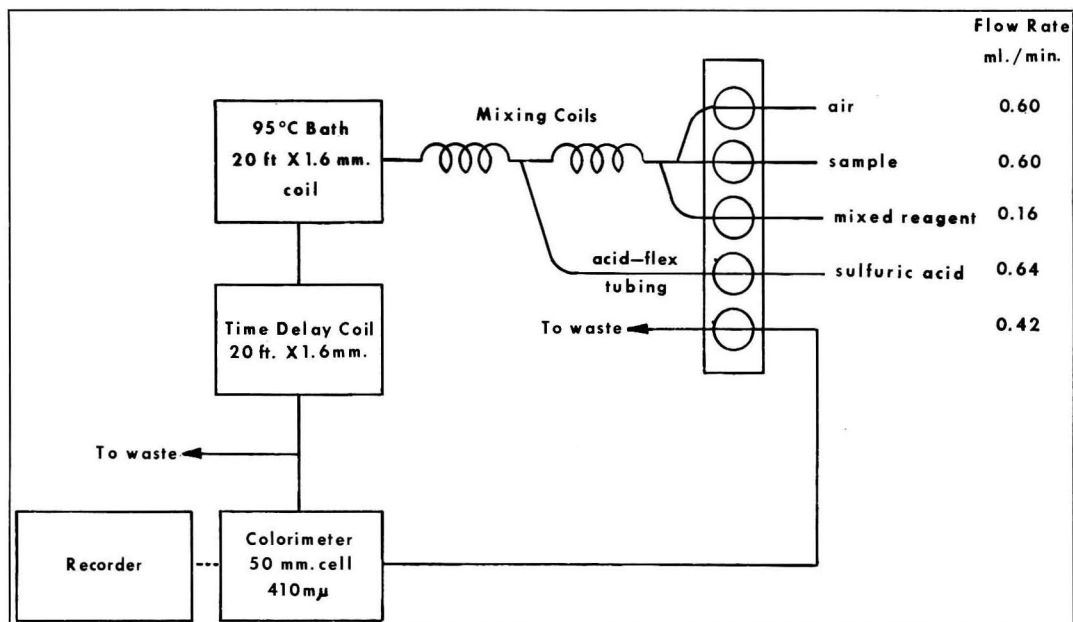
Figure 1. Automatic nitrate analysis flow diagram

Table I. Precision of the Nitrate Method

(Nitrate nitrogen, mg. per liter)

Number of Replicates	Procedure	Mean	Range	Standard Deviation	Coefficient of Variation, %
19	Automated	0.080	0.065–0.088	0.0051	6.4
20	Automated	0.265	0.250–0.277	0.0062	2.3
13	Automated	0.447	0.427–0.460	0.0088	2.0
24[a]	Manual	0.341	0.317–0.378	0.015	4.4
25[a]	Manual	0.552	0.522–0.582	0.018	3.3

[a] These results were obtained by the recommended procedure described by Kahn and Brezenski (1967).

accuracy of the method was verified by the authors (Kahn and Brezenski, 1967), who modified the procedure to obtain more reproducible analytical calibration curves, which obey the Beer-Lambert relationship.

This modified procedure was readily adapted to automation on the Technicon AutoAnalyzer with gratifying results, analyzing from 0.05 to 0.6 mg. of NO_3-N per liter with a standard deviation of less than 0.01 mg. of NO_3-N per liter—a twofold increase over the precision obtained by the nonautomated procedure. This method is preferred for the determination of nitrate because it eliminates the capricious reduction step which is an integral part of the other methods, and it more rapidly analyzes nitrate directly. Although the method when applied to filtered samples analyzed in this study gave accurate and precise results, it is expected to be subject to interference by streams adsorbing in the 410-mμ region and by turbidity. For such cases, a preliminary cleanup step would be required.

Experimental

Apparatus. The AutoAnalyzer components are as follows: proportioning pump; constant temperature bath, 95° C., containing a 12-meter × 1.6-mm. heating coil. Make all connections with acid-flex tubing; constant temperature bath, 30° C., with a 3-meter × 1.6-mm. time delay coil. Make all connections with acid-flex tubing; colorimeter, with 50-mm. tubular flow cell and 410-mμ filter; automatic sampler, operated at 2 minutes per sample and containing alternate tubes of distilled water and sample or standard.

Reagents. SOLUTION *A*. Dissolve 1 gram of brucine sulfate and 0.1 gram of sulfanilic acid in 70 ml. of hot distilled water and 3 ml. of concentrated hydrochloric acid. Cool. Dilute to 100 ml. The solution is stable for several months in a refrigerator.

SOLUTION *B*. Dilute 300 grams of sodium chloride (analytical grade) in 1 liter of distilled water.

MIXED REAGENT. Mix 100 ml. of solution *A* with 400 ml. of solution *B* just prior to use.

SULFURIC ACID SOLUTION. Carefully add with vigorous agitation and cooling 1 liter of concentrated sulfuric acid to 250 ml. of distilled water. Protect from moisture by keeping container capped during storage.

SET OF STANDARD SOLUTIONS. These contain 0.05, 0.1, 0.2, 0.4, and 0.6 mg. of NO_3-N per liter.

Procedure. Connect the AutoAnalyzer equipment as shown in Figure 1. Establish base line at 100% *T* on the recorder by drawing distilled water and the reagents through the colorimeter. Insert a 0 aperture into the sample beam and adjust to zero on the recorder. Remove aperture and analyze samples and standards as indicated at a 2-minute sampling time per test tube. Determine concentration of nitrate in samples from an analytical calibration curve constructed with standards (concentration *vs.* absorbance or peak height).

Results and Discussion

A schematic of the manifold for the automated nitrate analysis is shown in Figure 1. Alternate samplings of distilled water and sample or standard are drawn at 2-minute intervals from an automatic sampler, such as the large sampler manufactured by Technicon Controls, which can dispense from 200 test tubes at one loading. The sample is segmented with air, combined and mixed with the mixed reagent, and subsequently treated with the concentrated sulfuric acid solution. All additions of sample and reagents are controlled by the proportioning pump and the indicated tubings. The reaction mixture is then passed through a time delay coil, immersed in a 95° C. bath, and a portion is drawn through
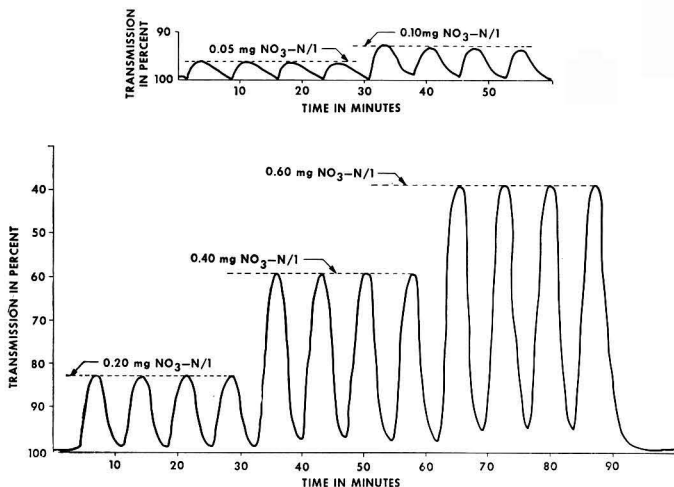
Figure 2. Spectrogram of automatic nitrate analysis at different concentration levels

Table II. Recovery of Added Nitrate Nitrogen from Various Samples by the Automated Nitrate Method

| | Milligrams per Liter | | | |
Sample	Original analysis	Amount added	Amount found	Recovery, %
A	0.165	0.100	0.255	90
		0.200	0.340	88
		0.300	0.460	98
B	0.195	0.100	0.270	75
		0.200	0.370	88
		0.300	0.470	92
C	0.192	0.100	0.292	100
		0.200	0.398	103
		0.300	0.501	103

the flow cell in the colorimeter—the color intensity measurements at 410 mμ are recorded on a strip chart recorder.

A typical set of spectrograms indicating the reproducibility of the procedure is shown in Figure 2. A more detailed description of the precision of the automated method is given in Table I. All samples were obtained from the Raritan River near the Victory Bridge where the average chloride content was 12,000 mg. per liter. Utilization of the automated brucine nitrate procedure improves the precision of the method roughly by a factor of 2.

To study further the efficacy of the automated method, known amounts of nitrate were added to estuarine samples. The samples were analyzed both before and after nitrate addition and recoveries of added nitrate were calculated. Some typical results are shown in Table II. As expected, recoveries compare favorably with those obtained by the manual method described by Kahn and Brezenski (1967). Although the recoveries range from 75 to 103%, all results are within three standard deviations of the expected analysis.

Literature Cited

Brewer, P. G., Chan, K. M., Riley, J. P., in "Automation in Analytical Chemistry, Technicon Symposia, 1965," p. 308, Mediad Inc., New York, 1966.
Britt, R. D., Jr., *Anal. Chem.* **34,** 1728 (1962).
Henriksen, A., *Analyst* **90,** 83 (1965).
Jenkins, David, Medsker, Lloyd L., *Anal. Chem.* **36,** 610 (1964).
Kahn, Lloyd, Brezenski, F. T., ENVIRONMENTAL SCI. TECHNOL. **1,** 488 (1967).
Kamphake, L. J., Hannah, S. A., Cohen, J. M., *Water Res. Intern. J.* **1,** 205 (1967).
Morris, A. W., Riley, J. P., *Anal. Chim. Acta* **29,** 272 (1963).
Mullin, J. P., Riley, J. P., *Anal. Chim. Acta* **12,** 464 (1955).
O'Brien, J. E., Fiore, J., *Wastes Eng.* **33,** 128 (1962).

Solvent Extraction of Phenol from Water with a Liquid Anion Exchanger

Frank X. Pollio, Robert Kunin, and Albert F. Preuss
Rohm and Haas Co., Philadelphia, Pa.

■ Amberlite XLA-3, a primary amine liquid anion exchanger, exhibits an appreciable capacity and selectivity for extracting phenol from water. Phenol can be conveniently stripped and recovered relatively pure from the saturated organic phase by distillation at a reduced pressure without carry-over of the extractant. Alternatively, the phenol-saturated organic phase may be brought in contact with a lime slurry which effectively restores the capacity of the resin for phenol extraction. The liquid anion exchanger seems ideally suited for the treatment of phenolic wastes.

Removal of dissolved phenolics from industrial waste waters has received considerable attention throughout the years (Amiot, 1933; Anderson and Hansen, 1955; Chaplin, 1932; Chasanov, Kunin, *et al.*, 1956; Crawford, 1926, 1927, 1927a; Dierichs, 1947; Kunin and Winger, 1962; Lowenstein-Lom, 1951; McKellar, 1958; Murdoch, 1946; Pollio and Kunin, 1967; Sargent and Graham, 1962). In the absence of any control, discharge of phenolic wastes into a water supply constitutes a serious source of pollution. As a consequence of increased production of phenolics, this problem is now of considerable concern. Of the numerous dephenolization methods that have been suggested, solvent extraction techniques appear to be preferred universally, particularly for wastes containing high concentrations of phenol. Besides having a better ability to handle concentrated phenolic wastes, solvent extractants generally show less tendency than solid adsorbents to be sensitive to variations in pH and phenol concentrations of the wastes being treated. Various solid adsorbent materials, including ion exchangers, have been found useful for dephenolization operations, but their effectiveness is often limited to the treatment of wastes containing relatively low levels of phenolics. In addition, the presence of certain foreign solutes usually reduces the efficiency of the over-all adsorption process.

Recent studies (Kunin and Winger, 1962) of Amberlite XLA-3, a primary aliphatic liquid amine, as a liquid extractant and liquid anion exchanger prompted the examination of this material for phenol extraction because it possesses many of the favorable attributes required of a liquid extractant.

Requirements for a Phenol Extractant

A solvent extrant seriously considered for dephenolization should meet certain basic requirements. Besides being a good solvent for phenol, it should be essentially insoluble in the waste itself and relatively inexpensive, so that extractant losses may be replenished at a modest expenditure. It should have a density sufficiently different from that of water to permit its separation from the raffinate by gravity and have a minimum tendency to emulsify with the phenol solution during the extraction process. The data in Table I indicate some of the basic properties of Amberlite XLA-3.

Experimental

Determination of Phenol Distribution Coefficients. The distribution coefficients for phenol were determined by contact of equal volumes of an organic extractant and deionized water containing varying concentrations of phenol. The extractions

Table I. Properties

Formula	Principally $tert$-$C_{18}H_{37}NH_2$ to $tert$-$C_{22}H_{45}NH_2$
Molecular weight	269–325
Neutral equivalent	353
Exchange capacity, meq./g.	2.5
Boiling point range, 760 mm.	295–325° C.
Specific gravity, 25° C.	0.848
Density, lb./gal., 25° C.	7.0
Refractive index, 25° C.	1.456
Viscosity, centipoise at 25° C.	22.0
Solubility	Relatively insoluble in H_2O (<20 mg./l.); soluble in common organic solvents. Excellent solubility in petroleum hydrocarbons

were performed in glass separatory funnels using mechanical agitation. After a 1-hour contact, the phases were permitted to settle for an additional 30 minutes, then separated by gravity. The raffinate (aqueous) phase was then analyzed colorimetrically for phenol by the 4-aminoantipyrine technique (Gottlieb, 1946) and the phenol concentration of the organic phase was obtained indirectly by difference. Distribution coefficients were finally calculated by dividing the phenol concentration of the organic phase after extraction by the concentration of phenol in the raffinate (aqueous) phase.

Screening of Extractants. Phenol distribution coefficients were measured for Amberlite XLA-3 and a selected group of extractants under similar experimental conditions (Table II). Distribution coefficients at different phenol concentration levels are tabulated in Table III.

Phenol distribution values were also determined for Amberlite XLA-3 dissolved in such solvents as deodorized kerosine (Shell Oil Co.), mineral seal oil (Atlantic Refining Co.), xylene, and a light oil (Tables IV and V). The light oil composition was 71% benzene, 23% toluene, and 6% xylene (meta and para) by volume.

Phenol Extraction as a Function of pH. The effect of pH on the phenol distribution coefficients for several extraction systems was investigated by adjusting a 4100-p.p.m. phenol solution to the desired pH by the addition of acid or base (HCl and NaOH). K_d values were measured for a 25% Amberlite XLA-3 solution in light oil and mineral seal oil, respectively. The pH's of the raffinates were also measured (Table VI).

Cyclic Study. The operating capacity of Amberlite XLA-3 for phenol realized during the treatment of a 4000-p.p.m. synthetic phenol water was checked through repeated contacts of a 400-ml. portion of a 20% solution in xylene with fresh 400-ml. portions of the synthetic phenolic water. Fifteen single-stage batch contacts were performed. After each extraction, the phases were allowed to separate and the raffinates were collected. The individual raffinates were subsequently analyzed for phenol (ultraviolet absorption at 269 mμ) and the distribution coefficients calculated. From the data in Table VII, it may be readily calculated that 13.7 grams (146.2 mmoles) of phenol were extracted by the 400 ml. of extracting solution. Utilizing the exchange capacity and specific gravity data for Amberlite XLA-3 (Table I), its available capacity in 400 ml. of the 20% extraction solution is found to be 169.6 meq. The amount of phenol extracted during the cyclic study, therefore, corresponds to a value in excess of 85% of the available capacity of the extractant.

Table II. Phenol Distribution Coefficients for Various Extractants at 25° C.

	Phenol, P.P.M.		
Extractant	Raffinate	Organic	$K_d{}^a$
Tributyl phosphate	<1.0	99.0	>99.0
Amberlite XLA-3[b]	20	980	49.0
Amberlite LA-2[b]	10	90	9.0
Amberlite XE-204[b]	11.5	88.5	6.4
Amberlite LA-1[b]	13.5	86.5	6.4
n-Butyl acetate	2.0	98.0	49.0
Isobutyl acetate	2.0	98.0	49.0
Ethyl acetate	3.5	96.5	27.5
2-Ethyl isohexyl acetate	3.5	96.5	27.5
5% (wt.) octylamine in light oil	49	951	19.4
Diisopropyl ether	9.0	91.0	10.1
Light oil	1370	2725	2.0
Benzene	34.2	65.8	1.9
Xylene	1450	2550	1.8
Toluene	36.0	64.0	1.8
Kerosine	84.0	16.0	0.2
Mineral seal oil	88.5	11.5	0.1

[a] Distribution coefficient, concn. organic/concn. aqueous.
[b] Liquid anion exchangers (Rohm and Haas Co.).

Table III. Phenol Distribution Coefficients for Undiluted Amberlite XLA-3

Phenol, P.P.M.				
Before Contact,	After Contact			
Aqueous	Aqueous	Organic	K_d	$K_d{}^a$
100	2	98	49.0	49.0
1000	20	980	49.0	49.0
4100	81	4019	49.6	49.6

[a] Calculated distribution coefficient (100% amine basis).

Table IV. Phenol Distribution Coefficients for Amberlite XLA-3

Vol. %	Phenol, P.P.M.			
in Kerosine	Aqueous	Organic	K_d	$K_d{}^a$
In Deodorized Kerosine				

Initial Phenol Content of Aqueous Phase = 100 P.P.M.

100	2.0	98	49.0	49.0
50	9.5	90.5	9.5	19.0
25	16.0	84	5.2	20.8
10	32.5	67.5	2.3	23.0
5	48.5	51.5	1.1	22.0
0	88.5	11.5	0.1	. . .

In Xylene				

Initial Phenol Content of Aqueous Phase = 4000 P.P.M.

100	79	3921	49.6	49.6
40	110	3890	35.3	88.3
20	210	3790	18.0	90.0
0	1450	2550	1.8	. . .

[a] Calculated distribution coefficient (100% amine basis).

Regeneration. It was found possible to regenerate Amberlite XLA-3 solutions previously exhausted with phenol by either vacuum distillation or treating of the spent extractant with a lime slurry. When vacuum distillation is used, phenol may be recovered in a relatively pure form. If phenol is to be recovered, Amberlite XLA-3 is used undiluted, or preferably diluted with a high boiling organic solvent. Mineral seal oil (Atlantic Refining Co.), which has a normal boiling point range between 250° and 360° C., was especially useful for this purpose. During an initial experiment using the undiluted resin, phenol was stripped from the extractant using a Podbielniak distillation column equipped with stainless steel packing at a pressure of 20 mm. of mercury. The distillation column was equivalent to less than 10 theoretical plates. Under these conditions, distillation of phenol from 90 ml. of Amberlite XLA-3, which contained approximately 8.5 grams of phenol, was studied. During distillation it was necessary to circulate steam through the distillation condenser in order to minimize any tendency for the phenol distillate to solidify in the condenser. Two 4-gram portions of snow-white phenol distillate, which solidified immediately at room

Table V. Phenol Distribution Coefficients

(Initial phenol content of aqueous phase = 4100 p.p.m.)

Vol. %	Viscosity, Cp.	Phenol, P.P.M. Aqueous	Phenol, P.P.M. Organic	K_d	$K_d{}^a$
In Mineral Seal Oil					
100	22.0	81	4019	49.6	49.6
50	9.2	200	3900	19.5	36.8
25	8.0	455	3645	8.0	32.0
10	. . .	1140	2960	2.6	26.0
0	6.3	3670	430	0.1	. . .
In Light Oil					
100	22.0	81	4019	49.6	49.6
50	3.2	114	3986	35.0	70.0
25	2.7	148	3952	26.2	104.8
10	. . .	325	3775	11.6	116.0
5	. . .	550	3550	6.5	130.0
2.5	. . .	825	3275	4.0	116.0
1	. . .	1150	2950	2.6	260.0
0	2.2	1370	2725	2.0	. . .

^{a} Calculated distribution coefficient (100% amine basis).

Table VI. Phenol Distribution Coefficients of 25% Amberlite XLA-3 as a Function of pH

pH Aqueous Before extraction	pH Aqueous After extraction	K_d
In Light Oil		
1.48	7.38	26.4
2.53	7.28	26.4
3.20	7.02	26.7
4.48	7.01	26.4
7.01	7.02	26.4
7.94	6.52	24.6
8.90	6.79	26.3
9.80	9.82	10.8
11.00	10.79	>10.8
In Mineral Seal Oil		
1.88	6.50	6.9
4.48	6.50	7.1
6.50	6.52	8.0
8.40	6.52	7.2

Table VII. Cyclic Study

Batch Contact	Phenol, P.P.M. Aqueous	Phenol, P.P.M. Organic	K_d
1	210	3790	18.0
2	375	3625	9.7
3	623	3377	5.4
4	863	3137	3.6
5	1125	2875	2.6
6	1365	2635	1.9
7	1600	2400	1.5
8	1900	2100	1.1
9	2100	1900	0.9
10	2350	1650	0.7
11	2450	1550	0.6
12	2650	1350	0.5
13	2630	1370	0.5
14	2700	1300	0.5
15	2700	1300	0.5

Table VIII. Phenol Distillation Data

Distillation Fraction	Distillate, Grams	B.P. Range, 20 Mm. Hg	$n_D^{45°\ C.}$	M.P., ° C.
1	$\cong 4$	86–88	1.5312	39–41
2	$\cong 4$	88–90	1.5152	36–38
Pure phenol	...	86	1.5348	41

Table IX. Phenol Extraction Data (15-Cycle Study)

Amberlite XLA-3 Solution	Cumulative Phenol Extracted, G./200 Ml.	Regeneration Efficiency, %[a]
Fresh	6.86	...
Regenerated, 100% of theory	6.16	90.0
Regenerated, 150% of theory	6.27	91.5

[a] Based on fresh phenol loading data.

temperature, were collected. Distillation data, including refractive indices and melting points of the distillate fractions, are reported in Table VIII.

Amines of this structure are heat-stable in the absence of air. In fact, Amberlite XLA-3 is prepared and fractionated at much higher temperatures than are employed for the recovery of phenol by distillation.

The possibility of regenerating Amberlite XLA-3 solutions with lime slurries was subsequently investigated using the 20% solution used to extract phenol during the cyclic study. The solution was divided into two equal 200-ml. portions and in turn brought in contact with equal volumes of an aqueous lime slurry. One portion was regenerated with a quantity of lime (0.364N) which corresponded to the quantity of phenol contained in the extractant; the other portion was brought in contact with a quantity of lime (0.546N) which corresponded to 1.5 times the stoichiometric phenolic content of the solution. The effectiveness of the lime regenerations was studied by contact of the regenerated amine solutions with fresh 4000-p.p.m. phenol solution. Fifteen batch treatment contacts were again performed with each of the regenerated solutions. The cumulative amount of phenol extracted by each of the regenerated solutions was then compared with the phenol extracted by 200 ml. of fresh solution under identical conditions (Table IX).

The 8 to 10% unaccounted phenol probably represents the phenol solubility in the organic extract phase. This solubility would be expected if the partition coefficient of xylene for phenol (Table II) is considered.

Discussion

Use of Amberlite XLA-3 as a phenol solvent extractant offers several advantages over most of the other materials screened for this purpose. From a practical standpoint, a favorable feature is the relatively high boiling point, which allows for the recovery of phenol through distillation, preferably at reduced pressures. In addition, if phenol recovery is not required, a lime slurry may be used to strip the phenol from the extractant. The ability to use lime for this purpose is noteworthy, since lime usually costs less than other appropriate alkali materials such as NaOH and ammonia. For wastes containing phenolics possessing a higher boiling point than phenol, the distillation method of stripping may not be satisfactory and therefore a chemical method may be required.

Though tributyl phosphate, n-butyl acetate, and several other materials screened all possessed K_d values greater than or equal to the distribution coefficient measured for Amberlite XLA-3, they have inherent drawbacks when considered as potential extractants for a phenol distillation recovery process. Their principal liabilities are appreciable solubilities and/or boiling points below or near the boiling point of phenol.

The phenol extraction characteristics of a 50% Amberlite XLA-3 mineral seal oil extractant offer a means of improving the viscosity of an Amberlite XLA-3 extractant. Phenol is recoverable by distillation, because of the high boiling point range of the mineral seal oil in question. The data in Table V indicate that the K_d values of several Amberlite XLA-3 solutions are still significant even at the higher dilutions, while viscosities are considerably improved. The phenol solvent extraction process for several systems is not adversely affected to any appreciable degree by traces of acid or alkali (Table VI).

The effect of solvent upon the partition coefficient of Amberlite XLA-3 solutions for phenol is significant. The aliphatic-type solvents such as kerosine and mineral seal oil, a kerosine-type material, have appreciably lower partition coefficients for phenol than the aromatic-type solvents. The net effect of using the aromatic type solvents as diluents is that the partition coefficient calculated for the pure amine of the extractant is not affected too adversely with dilution. In fact, the K_d values increase with dilution when xylene and light oil are the solvents. The ability of phenol to hydrogen bond to π electrons of aromatic hydrocarbons is recognized (Yoshida and Osawa, 1966) and may account for the greater than expected partition coefficients observed when Amberlite XLA-3 is diluted with these aromatic solvents.

For practical field use, Amberlite XLA-3 would preferably be used as 20 to 40% solutions. At higher concentrations, increased viscosities may cause some handling difficulties and entrainment losses may become significant.

Literature Cited

Amiot, R., *Compt. Rend.* **197**, 325 (1933).
Anderson, R. E., Hansen, R. D., *Ind. Eng. Chem.* **47**, 71 (1955).
Chaplin, R., *J. Phys. Chem.* **36**, 909 (1932).
Chasanov, M. G., Kunin, R., McGarvey, F. X., *Ind. Eng. Chem.* **48**, 305 (1956).
Crawford, R. M., *Ind. Eng. Chem.* **18**, 313 (1926).
Crawford, R. M., *Ind. Eng. Chem.* **19**, 168 (1927).
Crawford, R. M., *Ind. Eng. Chem.* **19**, 966 (1927a).
Dierichs, A., U. S. Patent **2,415,087** (1947).
Gottlieb, S., *Ind. Eng. Chem. Anal. Ed.* **18**, 16 (1946).
Kunin, R., Winger, A., *Angew. Chem.* (Intern. Ed.) **1**, 149 (1962).
Lowenstein-Lom, V., *Intern. Chem. Eng. Proc. Ind.* **32**, No. 5, 216 (1951).
McKellar, R., U. S. Patent **2,861,948** (1958).
Murdoch, D. G., *Trans. Inst. Chem. Engrs.* **24**, 90 (1946).
Pollio, F. X., Kunin, R., ENVIRONMENTAL SCI. TECHNOL. **1**, 160 (1967).
Sargent, R. N., Graham, D. L., *Ind. Eng. Chem. Proc. Design Develop.* **1**, 56 (1962).
Yoshida, Z., Ōsawa, E., *J. Am. Chem. Soc.* **88**, 4019 (1966).

Emission Spectrographic Determination of Barium in Sea Water Using a Cation Exchange Concentration Procedure

Barney J. Szabo[1] and Oiva Joensuu

Institute of Marine Sciences, University of Miami, Miami, Fla.

■ A concentration technique employing Dowex 50W cation exchange resin is described for the determination of barium in sea water. The separated barium is precipitated as fluoride together with calcium and strontium and measured by emission spectrographic analysis. The vertical distribution of barium in sea water has been measured in the Caribbean Sea and the Atlantic Ocean. The barium content varied between 7 and 23 μg. per liter; in two profiles, the lowest concentrations were at a depth of about 1000 meters.

The early measurements of barium content in sea water, using emission spectrographic analysis of ocean salt, revealed only the upper limits (Englehart, 1936; Black and Mitchell, 1952). Bowen (1956) employed a simplified ion exchange concentration technique using strongly acidic resin. The reported recovery was 88%; the ignited resin was analyzed by neutron activation. Chow and Goldberg (1960) and Chow and Patterson (1966) utilized an isotope dilution technique, with a mass spectrometer, for the measurement of sea water samples. Bolter *et al.* (1964) employed neutron activation analysis of the freeze-dried ocean salt. The strontium content in the sea water was assumed to be constant and was used as an internal standard. Turekian and Schutz (1965) reported the emission spectrographic analysis of sea water samples. The barium was coprecipitated with calcium and strontium oxalate. The recovery of barium determined using carrier-free Ba^{140} tracer varied from 50 to 70%; the coefficient of variation was about 25%. For duplicate determination, the stand-

[1] Present address, U. S. Geological Survey, Denver, Colo. 80225

ard error was 18%. Turekian and Johnson (1966) using the same method of concentration determined barium in sea water by neutron activation analysis. The coefficient of variation and standard error were reported to be the same.

In the work reported, the barium in sea water is concentrated using Dowex 50W-X8 cation exchange resin and hydrochloric acid as the eluting agent. The ion exchange procedure is monitored by utilizing a sensitive color test. The barium is precipitated as a fluoride together with calcium and strontium and is measured by using emission spectrographic analysis.

Experimental

Apparatus and Reagents. The ion exchange apparatus was designed for oceanographic use aboard ship. The upflow-type ion exchanger is described in Figure 1 with all the significant dimensions indicated.

All reagents were prepared with double-distilled water and were stored in polyethylene bottles. Hydrochloric acid solutions were prepared by bubbling HCl gas through distilled water. The cation exchange resin used was Dowex 50W-X8, 100 to 200 mesh. The reagents employed for the color test solution were: NaOH solution, 51% (J. T. Baker Chemical Co.), 320 grams diluted to 1 liter; Cal-Red indicator (Scientific Service Laboratory, Inc., Dallas) triturated with NaCl in 1 to 100 ratio; magnesium solution, 0.1M prepared from spectrochemically pure magnesium rods (Johnson, Matthey and Co., Ltd.) by dissolving the appropriate weight in a minimum amount of hydrochloric acid and diluting to volume; EDTA solution, 0.01M, prepared from the disodium salt of (ethylenedinitrilo)tetraacetic acid.

Procedure. The column was filled with the resin slurry allowing about 1 cc. for swelling which occurred when sea water passed through the column. The resin in the column was conditioned by passing 200 ml. of 5M HCl through it;
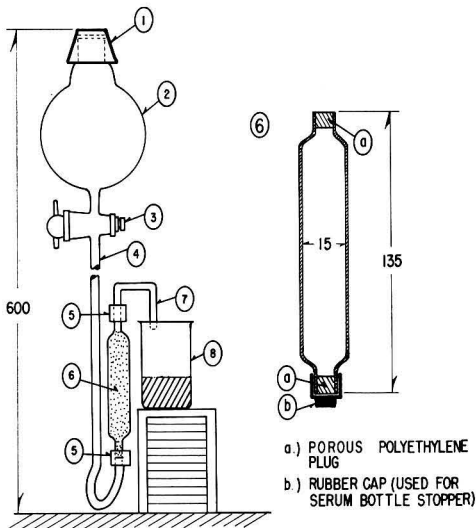
ION EXCHANGE APPARATUS
(ALL MEASUREMENTS IN MILLIMETERS)

① PLASTIC COVER ② 200ml SAMPLE RESERVOIR
③ TEFLON STOPCOCK WITH METERING VALVE (KIMBLE LABORATORY GLASSWARE) ④ CAPILLARY TUBING; 0.7mm INSIDE, 8 mm OUTSIDE DIAMETER
⑤ TYGON TUBING ⑥ ION EXCHANGE COLUMN
⑦ U SHAPED CAPILLARY ADAPTER ⑧ RECEIVING RECEPTACLE

a.) POROUS POLYETHYLENE PLUG
b.) RUBBER CAP (USED FOR SERUM BOTTLE STOPPER)

Figure 1. Ion exchange apparatus used for barium analysis

this was followed by a wash with 25 ml. of distilled water.

One hundred milliliters of distilled water, then 100 ml. of sea water samples were added to the glass bulk reservoir, and the diluted sea water was allowed to pass through with a flow rate of 0.6 ml. per minute. The bulb was rinsed with 25 ml. of distilled water, which was passed through the column.

The column was then eluted with $1M$ HCl solution. The first 100 ml. of the effluent, which eluted the alkali metals and major part of the magnesium (ascertained by EDTA titration), was discarded. The next portion of effluent of this preliminary elution was received in a beaker containing the color test solution (described below) until the change of color indicated the completion of the preliminary elution.

Preparation and Use of the Color Test Solution. To a tall-form 200-ml. beaker, 10 ml. of NaOH solution were added, followed by 10 ml. of $0.1M$ magnesium solution, and the mixture was stirred. One hundred milligrams of 1 to 100 mixture of Cal-Red indicator and NaCl were added next, and the mixture was stirred again; the solution was blue. To the above test solution, 5 ml. of $0.01M$ EDTA were also added —that is, a quantity sufficient to complex about 5% of the calcium content in sea water samples. The calcium content was calculated from the known chlorinity value using the Ca (mg./g.)/Cl (mg./g.) ratio of 0.0211.

The indicator (Patton and Reeder, 1956) changes color from pure blue to wine red at pH 12 to 14 when calcium is present. As little as 1×10^{-6} mmole of calcium produced a positively identifiable color change. The blue color of the pure indicator did not change when several millimoles of magnesium salt were added because of the immediate formation of the very insoluble $Mg(OH)_2$ precipitate.

Since the acidic effluent was neutralizing the blue-colored indicator solution continually, the pH was maintained between 11 and 14 by the addition of 5-ml. portions of NaOH solution. When the blue color of the indicator began to fade because of the dilution, another portion (about 100 mg.) of indicator mixture was added to the beaker and stirred. The change of the indicator color from blue to wine red signaled the first appearance of free calcium ions in the solution, and the preliminary elution was considered complete.

Final Elution and Chemical Processing. After the completion of the preliminary elution, the flow was stopped, and the column was eluted with 200 ml. of $5M$ HCl. The eluate was received in a 250-ml. Teflon beaker, evaporated to 2 to 3 ml., and transferred to an 8-ml. platinum crucible.

The solution was evaporated to 1 to 2 ml. then 0.5 ml. of concentrated HF was added and evaporated to dryness. The precipitate was ignited for a half hour at 500° C. in a muffle furnace. The crucible was cooled in a desiccator and weighed. The precipitate was scraped off with a platinum spatula and transferred to a small plastic vial for the spectrographic analysis.

Standards for the spectrographic analysis were prepared by mixing known amounts of $BaCO_3$ with barium free CaF_2. Yttrium was used as an internal standard (0.1% Y, 9.9% NaCl, 90% graphite). The standards and samples were mixed with internal standard and graphite in the ratio of 1:1:2 and filled in a $^1/_8$-inch electrode (Ultra Carbon Corp. Type No. 5790). Electrodes were burned with a 10-amp. arc in a 10% oxygen and 90% argon atmosphere using a Stallwood blower (Stallwood, 1954) in conjunction with a Bausch and Lomb dual grating spectrograph and Eastman I-F plates. Spectrum

Table I. Barium-133 Isotope Recovery from Sea Water Using Dowex 50W-X8, 100- to 200-Mesh, Ion Exchange Resin

Fraction Passing Through Column	Volume Collected, Ml.	Volume before Final Measurement, Ml.	Activity of 2 Ml. Test Solution, μc.	Activity of Total Fraction, μc.	Recovery of Individual Fraction, %
First effluent[a]	0–230	8	$<2 \times 10^{-5}$	$<8 \times 10^{-5}$	<0.0016
Second effluent[b]					
A	0–150	8	$<2 \times 10^{-5}$	$<8 \times 10^{-5}$	<0.0016
B	150–210	20	$<2 \times 10^{-5}$	$<4 \times 10^{-4}$	<0.008
Third effluent[c]					
a	–27	2	$<1 \times 10^{-4}$	$<1 \times 10^{-4}$	<0.002
b	28–52	25	5.7×10^{-3}	7.12×10^{-2}	1.42
c	53–54	2	3.60×10^{-2}	3.60×10^{-2}	0.72
d	55–79	25	2.60×10^{-1}	3.25	65.0
e	80–81	2	3.60×10^{-1}	3.60×10^{-1}	7.20
f	82–106	25	1.02×10^{-1}	1.275	25.5
g	107–108	2	5.7×10^{-3}	5.7×10^{-3}	0.11
h	109–135	2	7.0×10^{-3}	7.0×10^{-3}	0.14
i	136–162	2	$<1 \times 10^{-4}$	$<1 \times 10^{-4}$	<0.002
j	163–200	2	$<1 \times 10^{-4}$	$<1 \times 10^{-4}$	<0.002
Fourth effluent[d]	0–200	2	$<1 \times 10^{-4}$	$<1 \times 10^{-4}$	<0.002
Resin ignited	. . .	. . .	. . .	$<1 \times 10^{-4}$	<0.002
				Total 5.005	100.09

[a] Primary exchange, 100 ml. sea water and 100 ml. distilled water containing barium tracer passed through the column followed by 30-ml. wash.
[b] Preliminary elution, alkali metals, Mg and 25% of Ca content eluted with $1M$ HCl.
[c] Final elution, 200 ml. of $6M$ HCl eluent passed through the column.
[d] Another aliquot of 200 ml. of $6M$ HCl eluent passed through the column.

lines Ba 4554.042 A. and Y 4398.011 A. were used. The detection limit for barium is about 1 p.p.m. The precision of the duplicate determinations above 5 p.p.m. of Ba was $\pm 10\%$, or better.

Efficiency of Barium Recovery from Sea Water by Cation Exchange Resin. The efficiency of the ion exchange concentration method of barium in sea water was investigated radiometrically using Ba^{133}, a gamma emitting radionuclide with a half life of 7.5 years. A thallium-activated sodium iodide scintillation detector (5×5-cm. crystal with 1.5-cm. diameter and 4-cm. deep well) was used with a Nuclear Data multichannel analyzer. The Ba^{133} was obtained from Nuclear Science and Engineering Corp.; the specific activity was 2060 mc. per gram of barium and its radiochemical purity was better than 99%.

Dilutions of the standards and unknowns were counted in 3-ml. test tubes; 2 ml. of solutions were used. All counts were made to include the 302- and 355-k.e.v. photopeak doublet; total counts ranged from 100,000 to 2,500,000.

An aliquot of 5 μc. of Ba^{133} tracer was added to the mixture of 100 ml. of distilled water and 100 ml. of sea water. The solution was passed through the ion exchange resin and was eluted as described previously. The effluent was collected, evaporated, and counted. The data are summarized in Table I.

The barium loss was negligible during the primary exchange on the resin and during the preliminary $1M$ HCl elution. On the other hand, barium was quantitatively recovered from the column using 200 ml. of the $5M$ HCl eluent. Over 99.9% of the Ba^{133} isotope adsorbed on the column was recovered between the 25th and 130th ml. of effluent—i.e., between 1 and 7 column volumes of the eluting agent.

Sampling Procedure. Five-liter all plastic [poly(vinyl chloride)] bottles were used to obtain the sea water samples. These bottles were equipped with reversing protected and unprotected thermometers which are standard equipment to ascertain sampling depths. The sampling bottles close to the sea floor were positioned by a pinger which was attached to the wire rope. A sample of 0.5 liter was withdrawn from each bottle as soon as it was raised to the surface. The barium samples were processed on board within 10 hours with the exception of a sample collected at station C-18 (Table II).

Results and Discussion

The completeness of barium exchange from sea water and its quantitative elution with hydrochloric acid was demonstrated in the previous section. The over-all accuracy of the ion exchange method and spectrographic analysis was investigated by the measurements of known amounts of barium added to barium-free calcium carbonate carrier and to sea water aliquots, the barium content of which was previously ascertained.

The results of the recovery experiments are presented in Table III; the relative error ranged between -22 to $+5\%$, the per cent standard error was ± 13.5. The duplicate and quadruplicate determinations of sea water samples (Table II) were reproduced within $\pm 11\%$ with the exception of a sample collected at station C-18.

Analysis of Samples. The results of the barium analysis are presented in Table II. The vertical distribution of barium in the Caribbean Sea and neighboring Atlantic Ocean waters varied from 7 to 23 μg. per liter. The lowest barium concentra-

Table II. Barium Contents in Sea Water Samples

Station	Location	Bottom Depth, Meters	Sampling Depth, Meters	Barium Measured,[a] µg./L.	Barium Average, µg./L.
C-20	19° 35′ N	8260	5	13.8[b] 17.3	16
	68° 22′ W		1000	6.6[b] 7.0	7
			3000	22.7	23
			5900	14.2[b] 17.6	16
C-19	20° 35′ N	2800	700	15.2	15
	74° 10′ W		1500	17.0	17
			1800	18.2	18
C-18	18° 30′ N	2630	700	14.5	14
	76° 10′ W		1200	9.0[b] 13.8[b]	11
C-14	15° 45′ N	4250	1	16.8	17
	73° 50′ W		140	16.1	16
			660	16.6	17
			950	11.0	11
			2400	19.6	20
			3350	19.6	20
			4020	14.9	15
A-4	26° 20′ N	4736	4720	17.9	18
	76° 20′ W		4729	23.4	23
C-16	17° 40′ N	4300	~2000	11.4 14.2	14
	73° 20′ W			15.0 15.2	

[a] All samples are corrected for the barium content in the HF reagent used (0.02 µg./0.5 ml.).
[b] Analyzed about one year after collection whereas all other samples were processed a few hours after sampling.

Table III. Results of Barium Recovery Experiments

Sample	Barium Originally Present, µg.	Barium Added, µg.	Barium Measured, µg.	Relative Error, %
a	0	. . .	<0.06[b]	. . .
c	<0.06	0.92	0.79	−14
c	<0.06	2.30	2.36	+ 3
d	1.04 ± 0.05	0.46[e]	1.17	−22
d	1.04 ± 0.05	0.92[f]	1.87	− 5
d	1.04 ± 0.05	2.30[g]	3.50	+ 5
h	. . .	. . .	8.10[i]	. . .

[a] 100 mg. of $CaCO_3$ dissolved in minimum amount of HCl, 0.5 ml. HF added, and evaporated to dryness.
[b] Average of four individual measurements.
[c] 100 mg. of $CaCO_3$ dissolved in HCl, diluted to 100 ml., barium tracer added and solution passed through the column.
[d] An aliquot of 100 ml. of sea water containing 1.04 ± 0.05 µg. of Ba diluted with 100 ml. of distilled water, barium tracer added and solution passed through the ion exchange column.
[e] 1.50 ± 0.05 µg. total barium in sample.
[f] 1.96 ± 0.05 µg. total barium in sample.
[g] 3.34 ± 0.05 µg. total barium in sample.
[h] 200 ml. of HF (59%) evaporated to 2 ml., 100 mg. of $CaCO_3$ added and evaporated to dryness.
[i] 0.5 ml. of HF was used for the precipitation of Ca, Sr, and Ba as fluoride in sea water; 0.5 ml. contained 0.02 µg. of barium.

tion was at a depth of 1000 meters in the Puerto Rico Trench. The barium content in the Colombian basin varied between 11 and 20 µg. per liter; the lowest content occurred at a depth of 950 meters. Similar range of barium content was shown by Chow and Patterson (1966); and Turekian and Johnson (1966) in the North Atlantic waters. Interestingly, the depth of barium minimum content coincides with the depth of dissolved silicate maximum (Richards, 1958).

Acknowledgment

Literature Cited

Black, W. A., Mitchell, R. L., *J. Marine Biol. Assoc. U.K.* **30,** 575–84 (1952).

Bolter, E., Turekian, K. K., Schutz, D. F., *Geochim. Cosmochim. Acta* **28,** 1459–66 (1964).

Bowen, H. J. M., *J. Marine Biol. Assoc. U. K.* **35,** 451–60 (1956).

Chow, T. J., Goldberg, E. D., *Geochim. Cosmochim. Acta* **20,** 192–8 (1960).

Chow, T. J., Patterson, C. C., *Earth and Planetary Sci. Letters* **1,** 397–400 (1966).

Englehart, W., von, *Chem. Erde* **10,** 187–246 (1936).

Patton, J., Reeder, W., *Anal. Chem.* **28,** 1026–28 (1956).

Richards, F. A., *J. Marine Res.* **17,** 449–65 (1958).

Stallwood, B. J., *Opt. Soc. Am.* **44,** 171–6 (1954).

Turekian, K. K., Johnson, D. G., *Geochim. Cosmochim. Acta* **30,** 1153–74 (1966).

Turekian, K. K., Schutz, D. F., *Occasional Publ.* No. **3,** Narragansett Marine Laboratory, 41–89 (1965).

Apparatus for Automatic pH Control in Algal Cultures

Fred V. Soltero[1] and G. Fred Lee

Water Chemistry Laboratory, University of Wisconsin, Madison, Wis. 53706

■ An electronic pH controller has been designed and tested for the control of pH in algal cultures. The output of a laboratory pH meter is used to control the addition of a CO_2-air mixture to the culture. The apparatus controlled the pH of 7, 8, and 9 of cultures of *Scenedesmus quadricauda* to ± 0.1 pH unit.

V arious investigators (Gerloff, Fitzgerald, *et al.*, 1950; Osterlind, 1949; Zehnder and Gorham, 1960) have used different ways to control the pH of an algal culture in order to determine the optimum growth under specific experimental conditions. These methods include manual addition of acid or base to the culture medium at constant time intervals, addition of large amounts of pH buffers, such as Tris, aeration with CO_2-enriched air at different partial pressures, and the use of chemical species that, upon utilization, tend to counteract the normal pH changes in solution. In general, these procedures either do not provide precise pH control or require the addition of large amounts of compounds to the medium. This paper describes the construction and operation of a relatively inexpensive apparatus that will provide precise pH control in algal cultures.

Experimental Methods and Materials

Figure 1 is a schematic diagram of the culture apparatus used in this investigation. The pH meter was a Beckman Zeromatic pH meter. A combination glass-calomel electrode was inserted into the culture vessel, which was a 4-liter borosilicate bottle with two perforations on its shoulder. The culture vessel was placed on a wooden frame above a

[1] Present address, College of Agriculture and Mechanic Arts, University of Puerto Rico, Mayaguez, Puerto Rico.

Figure 1. Schematic diagram of culture system with automatic pH control

Figure 2. Schematic circuit diagram for automatic pH controller used with the Beckman Zeromatic pH meter

variable-speed 1/100-hp. shaded pole motor (Dayton Electrical Manufacturing Co., Chicago, Ill.) with a permanent magnet attached to the shaft. The rate of stirring was controlled by a Variac transformer. The culture was illuminated with a circular 32-watt fluorescent lamp placed around the middle of the bottle. The culture vessel was stoppered with a solid rubber stopper through which three glass tubes were inserted; one extended to the bottom of the vessel with a diffuser stone attached for the CO_2-air supply, another tube extended about halfway down from the top of the liquid and was used for sampling, and the third short tube served as the escape route for the gas mixture to the atmosphere. The CO_2-air mixture was passed through a sterile cotton filter to remove any contaminants.

A Rustrak recorder, 100-μa. full scale, was connected to the pH meter to provide a record of culture pH.

The automatic pH controller was an electronic device constructed in this laboratory to control the solenoid on the CO_2-air supply line. Figure 2 is a schematic circuit diagram of the automatic pH controller. The input signal for the auto-

matic controller was taken from the cathode of the output tube of the pH meter. Initially, the system was balanced at the desired set value. Under these conditions, no output voltage difference was obtained from the two channels of the d.c. amplifiers on the controller. When there was a slight difference in the pH value from the preset value, an output voltage was obtained from the amplifiers. The voltage caused a transistor to turn on the current through the relay which opened or closed the solenoid valve installed in the CO_2-air supply lines. Thus, whenever algal utilization of CO_2 resulted in an increase in medium pH, the controller opened the CO_2-air line and the gas mixture bubbled through the medium until the pH was restored to its original value. An interval timer was attached to the controller to register the total open time of the solenoid.

The CO_2-air mixture was fed at a rate of approximately 1400 cc. per minute measured at 1 atm. and 25° C. At pH values less than 9, 5% CO_2 in air, by volume, was found to be satisfactory. At pH 9, 2% CO_2 in air was used. The maximum variation of pH in the culture medium was ±0.1 pH unit.

Figure 3. Growth curves of *Scenedesmus quadricauda* in Gorham's medium with automatic pH control

Figure 4. Effect of pH on growth of *Scenedesmus quadricauda* in Gorham's medium

The design of the controller is a modified version of a circuit provided by M. J. Johnson, University of Wisconsin, Department of Biochemistry. The total cost of the controller was about $100.

A unialgal culture of *Scenedesmus quadricauda* (Indiana Culture Collection No. 77) was used to test the automatic controller. All external connections of the culture vessel were plugged with cotton and the unit was autoclaved for 30 minutes at 15 p.s.i. Gorham's medium (Hughes, Gorham, *et al.*, 1958) was used in all experiments and the temperature of the culture medium was maintained at 23° C.

Growth in the cultures was determined by an increase in absorbance of the solution measured at 600 mμ in a Bausch and Lomb Spectronic 20 spectrophotometer. An absorbance of 1.86 yielded 1.45 grams per liter of dry weight.

Results and Discussion

Figure 3 presents the growth curves for *Scenedesmus quadricauda* in Gorham's medium at pH values of 6.0, 7.0, 8.0, and 9.0. Examination of this figure shows that 2 to 5 days after initiation of the run, the cultures entered into an apparent log growth phase. During the log growth phase, the demand for the CO_2-air mixture was fairly frequent. At pH 8.0, the automatic controller fed CO_2-air mixture at approximately 10-minute intervals. The maximum deviation from the preset pH value during the run was ±0.1 unit. The slopes of the growth curves during log phase can be used as an index of the effect of pH on growth. These slopes are plotted against pH in Figure 4. The apparent optimum growth for the organism in the pH range 6 to 9 is at pH 7. Further studies are needed to verify these results, since only single runs were made at each pH. These results demonstrate the applicability and reliability of the pH controller for studies on the growth of algae at constant pH.

Literature Cited

Gerloff, G. C., Fitzgerald, G. P., Skoog, F., "The Isolation, Purification, and Nutrient Solution Requirements of Blue-Green Algae," Symposium on the Culturing of Algae, pp. 27–44, Charles F. Kettering Foundation, Dayton, Ohio, 1950.

Hughes, E. O., Gorham, P. R., Zehnder, A., *Can. J. Microbiol.* **4**, 225–36 (1958).

Osterlind, S., *Symbolae Botan. Uppsalensis* **10**, 10–31 (1949).

Zehnder, A., Gorham, P. R., *Can. J. Microbiol.* **6**, 645–60 (1960).

NEW PRODUCTS DIGEST

Turbidity-to-Current Converter

A turbidity-to-current converter is now available for use with the Foxboro Model 32 Turbidimeter. The all solid-state, high impedance device converts a 0 to 100 mv. d.c. signal from the turbidimeter to a 10- to 50-milliamp d.c. signal that is compatible with a Foxboro electronic line of recorders, controllers, and alarms. The converter is weather-proof, operates from $-20°$ to $+140°$ F., and can be located several thousand feet from the turbidimeter. Foxboro Co. **60**

Acrylic Plastic Valves

A series of multiport Plexiglas valves, designed to avoid the high corrosion rate that is often experienced by metal valves used in water treatment equipment, is impassive to the salts of active metals. The valves are lightweight and easy to handle and are made in pipe sizes from $1^1/_2$ inches to a 4-inch flanged model. Graver Water Conditioning Co. **61**

Automatic Sampler

A compact, portable, automatic unit for sampling water or waste water, the sampler can obtain up to 24 samples at regular intervals. Samples are stored in a cooled, insulated chamber. The device works on a vacuum principle, does not require outside power or batteries, and is constructed of materials which will not alter corrosive liquids. Serco Laboratories. **62**

Silver-Zinc Battery

A D-size, rechargeable, sealed, silver-zinc battery is capable of undergoing hundreds of discharge-recharge cycles, delivers 32 watt hours per pound and 2.7 watt hours per cubic inch, and performs well at both high and low temperatures (100% capacity at $125°$ F., 75% capacity at $32°$ F.). The cell has a long shelf life in charged condition (85% capacity after 6 months, 70% after 1 year). Yardney Electric Corp. **63**
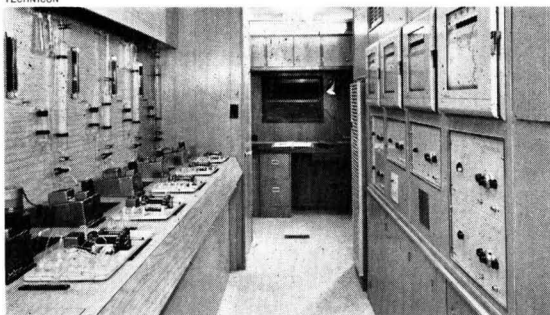
Pollution Monitoring Goes Mobile

Already outfitted or modified for special purposes, the Beckman air sampling laboratory (circle **64**) and the Technicon unit (circle **65**) can easily be moved to new locations to monitor a variety of air pollutants. Chromalloy American Corp.'s vehicle emissions mobile test lab (circle **66**) analyzes car exhaust. Honeywell makes a mobile monitor (circle **67**) complete with generator, for water quality measurements. The three units shown here were demonstrated at APCA's annual meeting in Cleveland, Ohio, earlier this month.

Alumina-Coated Sheet with Fluorescent Indicator

The addition of the fluorescent indicator to the precoated alumina sheet improves the effectiveness and increases the range of thin-layer chromatography as an analytical tool. Like the previous alumina form of Chromagram Sheet 6062 without fluorescent indicator, Chromagram Sheet 6063 consists of an inert polyester base carrying a uniform coating of highly active alumina adsorbent. Eastman Kodak Co. **68**

Humidity Generator

A constant water level system balances the heat input to this humidity generator to create vapor migration from the generator to the workspace on a balanced temperature level. The device provides for continuous modulation of water supply and is metered to balance the rate of vapor generation required by the wet bulb control instrumentation. Available in three standard sizes, with variable heat input (300 watts to 3 kw.). Tenney Engineering, Inc. **69**

Flame-Emission Spectrometer

A specialized hydrogen-entrained air burner system in this flame-emission spectrometer decreases the formation of oxides found in systems using compressed oxygen or air, thus improving reproducibility and sensitivity. The design allows drift-free high sensitivity determination of thermally excitable metals with little spectral interference. American Instrument Co., Inc. **70**

Indicator Papers

The Whatman-BDH indicator papers produce bright, distinct, stable colors for exact color matching between the paper strip and color chart. H. Reeve Angel & Co., Inc. **71**

Injection Marker

The Jimtronic injection marker makes it possible to obtain an accurate indication of the start of a chromatogram without introducing air (thus prolonging filament life in TC cells by eliminating oxygen from the sample) and to calculate average linear velocity when using a detector sensitive to air. Gow-Mac Instrument Co. **72**

Scoop-Type Sampler for Liquid Wastes

The rotating scoop on this sampler is designed to provide a sample representative of all depths of the flow under study. Scoops are available in cast aluminum, cast stainless steel, or Plexiglas. Accessories available include a time clock to reduce number of samples, a revolution counter, sample collectors, and the sample refrigerator. Lakeside Engineering Corp. **73**

Flow and Valve Slide Rule

A redesigned, 12-inch slide rule provides flow calculations quickly and conveniently. New functions include sizing of control valve trims and determination of Reynolds numbers, quadrant edge orifices, and suitable meter run sizes. New color codes and numbers are imprinted on the plastic heat-resistant rule. Foxboro Co. **74**

NEW LITERATURE
DIGEST

Fibers facilitate desalination

Hollow noncellulose fibers, each smaller than a human hair but capable of withstanding pressures of 600 p.s.i., are the heart of an experimental, reverse osmosis desalination and waste water treatment process recently revealed by Du Pont. About 20 million of these strong hollow fibers (i.d., 25 microns; o.d., 50 microns) are packed inside a permeator shell for each module of the system. The modular design allows for easy expansion of an installation.

The system uses a simple reverse osmosis process. Brackish water is pumped at high pressure (600 p.s.i.) against a membrane, which is, in reality, a multimembrane of very fine hollow fibers yielding surface areas as great as 50,000 to 80,000 square feet for a 7-foot $\times$ 12-inch diameter pipe module. Under pressure, part of the water passes into the bore of the fibers, leaving most of the dissolved salt and part of the water behind as brine. The water is collected from the bore of the fibers as product; the remaining salt and water are rinsed from the outside of the fibers in the normal operation of the system.

The process removes nonionized materials such as bacteria and detergents as well as ionized materials such as dissolved salts, and is suitable for pretreatment of industrial process waters, treatment of industrial wastes, waste water reclamation, and desalination of sea-water and brackish waters.

For further information on this patented process, circle No. 75 on the Readers' Service Card.

Sewerage. A 24-page illustrated booklet, *Understanding the World of Sewerage*, reviews waste handling methods and discusses modern needs and solutions to sanitary sewer problems. Can-Tex Industries. **76**

Chlorinated hydrocarbon pesticides. *The Identification and Measurement of Chlorinated Hydrocarbon Pesticides in Surface Waters* is now revised, updating the chapters on sample collection, gas chromatography, control of interferences, and sensitivity and specificity. Federal Water Pollution Control Administration. **77**

Air/water conservation bibliography. A 15-page *Subject Index to Current Literature on Air and Water Conservation* lists legal, economic, health, control, and other aspects of air and water conservation. Entries include basic subject category, title, and reference number, and a request form is attached to the document to facilitate location of original document. American Petroleum Institute. **78**

Organic chemicals supplemental listing. A supplement has been published to *Eastman Organic Chemicals, List. No. 44.* Over 150 chemicals made available since the above catalog was issued are listed. All are in stock for immediate delivery. Distillation Products Industries. **79**

Electrophoresis apparatus. A factsheet describes the latest advances in design of electrophoresis tanks. Colab Laboratories, Inc. **80**

Sodium borohydride. A 24-page brochure covers physical properties, handling, and analytical procedures of sodium borohydride as a reducing agent for organic functional groups. Ventron Corp. **81**

Glassware products. A 20-page illustrated brochure shows the manufacturing facilities and exclusive products of a 20-year-old glassware firm, as well as more general products offered. Lurex Manufacturing Co. **82**

Formulating coatings for Rule 66. A 23-page bulletin, *Reformulating Coatings to Conform to Air Pollution Control Legislation,* lists the major considerations in reformulating coatings and shows how Dowanol glycol ethers can serve in the new formulations. A series of graphs demonstrates the solubility of commonly used coating constituents in various solvents. Dow Chemical Co.   **83**

Corrosion and scale control. Reprint No. 162 gives detailed operating data on two types of chemical treatment and alternate system design and disposal methods. The paper, on the topic of controlling corrosion and scale in a cooling system while maintaining strict pollution control over tower blowdown, gives schematic layouts, tables, and cost figures. Nalco Chemical Co.   **84**

Condensation nuclei counter. A factsheet describes this instrument for measuring the number concentration of airborne nuclei. A bibliography of research articles is included. Singco, Inc.   **85**

Industrial waste problems. A folder describes the services available in deep well drilling, subsurface liquid waste disposal, and the like. International Disposal Contractors, Inc.   **86**

Granular activated carbon products. Bulletin 20-2 describes products designed to remove organic contaminants from municipal or industrial waste water and the adsorption design guidelines for their application. The new products are coal-based carbons with high surface areas and pore structures carefully controlled for adsorption of both high and low molecular weight impurities. Bulletin 20-4 illustrates three basic adsorber configuration designs, and includes graphs depicting head loss characteristics and expansion of the granular carbon bed in backwashing. Calgon Corp.   **87**
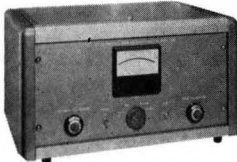
Packaged plant air system. A 4-page booklet lists the features of a two-stage, water-cooled, single frame-mounted packaged plant air system available in four ratings. Allis-Chalmers.   **88**

Oxygen recovery by streams. A technical report, *The Aeration Capacity of Streams,* details how to judge the ability of virtually any river in the U. S., to reaerate. The new prediction method is based on the hydraulic properties of rivers, from information gathered by Geological Survey's Water Resources Division. Geological Survey.   **89**
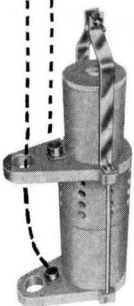
Automatic cold trap filler. A 4-page bulletin describes a liquid nitrogen level control system for use in automatic filling of cold traps, for use in either laboratory-type or self-pressurized dewars. Complete operating characteristics, detailed specifications, and prices are included in the bulletin. International Controls Corp.   **90**

Electrochemistry and membrane processing. A 26-page brochure outlines proprietary developments in chemistry, new processes, water desalting, and electronics. Discussed are water, food and chemical technology, research, and electronics. Ionics, Inc.   **91**

BOOKSHELF

The Rising Cost of Water

By Edwin S. Mills

This volume contains the 26 papers presented at the seventh Western Resources Conference, held during the summer of 1965. The scope of the volume is impressive; it surveys the current state of research in virtually every discipline concerned with water. The papers are grouped under six major headings: Issues in Theoretical Economic Analysis, Case Studies of Water Management, Studies of Water Reallocation, Political and Administrative Studies, Research on Hydrology and Engineering, and Major Research Programs and Needs.

In a volume authored by so many research workers, diversity in approach and quality is inevitable. Some papers survey the current state of research in a particular area. Others present new applications of research tools to substantive problems. Still others, comprising part of the last section of the book, attempt to outline areas of needed research. This latter group is the least satisfactory from this reviewer's point of view. I find it generally unrewarding to read agendas of research that ought to be carried out if money, personnel, data, or techniques were available.

The contributors to this volume include economists, political scientists, lawyers, engineers, and others. It would be pretentious for me to attempt a critical evaluation of papers in fields far from my own competence, and space would not permit discussion of all 26 papers. Suffice it to say that I found several of the papers having to do with hydrology, law, and politics to be interesting and instructive. I shall restrict my further remarks to a small arbitrarily selected group of papers on subjects to which my expertise extends.

The first paper in the book is a masterful survey by Kenneth Arrow of the current state of economists' thinking on some very difficult matters having to do with discounting and public investment. It should be instructive to noneconomists interested in water resource investment, and contains material that will be new to most economists, as well.

The second paper is a reprint of a well known piece by Peter Steiner on the role of alternative cost in public investment. It was originally published in the *Quarterly Journal of Economics* and appears to be the only previously published paper in the volume.

There follows a very interesting paper by Joe S. Bain concerning the role of local, state, and Federal Government in California's water resource development. The paper provides another chapter in the dreary story of resource misallocation by public authorities in irrigation projects. Although detailed analysis is missing from the paper, the evidence strongly suggests that federal irrigation projects have been badly misconceived in California.

Robert K. Davis provides a perceptive analysis of alternative methods of maintaining desirable levels of dissolved oxygen in the Potomac estuary. He compares the cost of implementing the Corps of Engineers' proposals for low flow augmentation with the cost of various forms of effluent treatment, effluent diversion, and reaeration. His calculations suggest that low flow augmentation is a very expensive way of maintaining water quality in the Potomac estuary. This paper provides further evidence of the damage that can be done by giving major responsibility for water quality to an agency whose major activity is the construction of dams and reservoirs.

Recreational benefits

There is an interesting paper by Paul Davidson, F. Gerard Adams, and Joseph Seneca on measurement of recreational benefits from improved water quality. To the best of my knowledge, this is the first attempt at empirical estimation of such benefits. Since recreational benefits are likely to be crucial in justifying improved water quality, this is a welcome addition to the available literature.

In a provocative paper, Arthur Maass attacks economists' use of benefit-cost analysis in evaluating water resource projects. His argument is that the major limitation of benefit-cost analysis is that it neglects income redistribution benefits because it is based on the "new welfare economics" which is "indifferent to income distribution." To say that the new welfare economics is indifferent to income distribution is simply ridiculous. Modern welfare economics is very concerned with the distinction between measures to increase the size of the pie and those to cut it differently. But no significant writer on welfare economics would say that either the size of the pie or the way one slices it is a matter of indifference.

A suspicion—and a challenge

One reason for economists' concern with the efficiency of public investment projects is that the government (both the legislature and the administration) says that projects are supposed to be justified on efficiency grounds. Moreover, many economists have a suspicion, which I share, that the redistributive effects of many government programs are in favor of groups who happen to be powerful enough to use the government programs for their own profit, rather than disadvantaged groups who have a strong claim on government assistance. The redistributional effects of water resource programs mostly

benefit landowners since the benefits show up in land values. Many would doubt that these people have strong claims for government assistance. If that example is unconvincing, I invite Mr. Maass to study the redistribut:onal effects of the federal oil import control program!

The Third Wave. . . America's New Conservation. Conservation Yearbook No. 3. U. S. Department of the Interior. 128 pages. U. S. Government Printing Office, Washington, D. C. 20402. 1967. $2.00, paper.

The Conservation Yearbook Series constitutes both the annual reports and special reports to the nation by the Department of the Interior. Twenty-six subdivisions of the department are included in this volume, including the Bureau of Indian Affairs, the Water Pollution Control Administration, the Office of Saline Water, and others of interest to environmental specialists. The photography is exquisite, the presentation artistic, and the volume is certain to appeal to nature lovers throughout the country.

Automobile Disposal: A National Problem. U. S. Bureau of Mines. viii + 569 pages. U. S. Government Printing Office, Washington, D. C. 20402. 1967. $4.50, paper.

Case studies of automobile graveyards in 54 communities throughout the U. S. showed 85 distinct factors which have relevance to the junk automobile blight. Inadequate licensing and zoning regulations contribute heavily to the problem, as do the methods used in making steel. The study shows that there are a variety of ways not presently being used in many areas by which inventories of junk automobiles could be reduced and held to a minimum level.

Water Resources Thesaurus. U. S. Department of the Interior. xi + 237 pages. U. S. Government Printing Office, Washington, D. C. 20402. 1966. $2.00, paper.

Developed in response to section 300 of the Water Resources Research Act, wherein the Secretary of the Interior is directed to assure that the programs authorized in the act will supplement and not duplicate established water research programs, this thesaurus will be particularly valuable to the professional indexer, to the author who is requested to provide index terms along with an abstract of his paper or report, and to the principal investigator who is asked to suggest "key words" to accompany his Notice of Research Project (NRP).

The format of the book should simplify location of the descriptors which are sought. Section I, "Descriptors and Cross References," is the largest portion of the book. Terms are listed alphabetically there along with broader terms, narrower terms, and related terms. Section II is a listing of the descriptors by groups, showing their relationships to the categories and subcategories of the Committee on Water Resources Research, Federal Council for Science and Technology. By scanning terms listed in this section under one of the groups in the general subject area, the user will be able to choose terms to pursue in Section I. Finally, Section III is a simple alphabetical listing of all descriptors, providing a quick reference for checking spelling and word forms. The work is meant to "improve communications and facilitate retrieval of scientific and technical information."

Atmospheric Humidity Atlas—Northern Hemisphere. Irving I. Gringorten *et al*. Air Weather Service Technical Report No. 191. x + 144 pages. Air Force Cambridge Research Laboratories, L. G. Hanscom Field, Bedford, Mass. 01730. 1966. No charge, paper.

A comprehensive study of atmospheric humidity, the atlas contains 120 plates devoted to isopleths of water vapor mixing ratios and dew points over the Northern Hemisphere. Data were drawn from 1500 surface observational sites and 400 upper-air radiosonde stations, with dew point records kept for five years at each point. The duration of both normal and abnormal periods of humidity can be calculated from the data used in conjunction with a theoretical model of atmospheric humidity recently developed by Gringorten.

Proceedings of the National Symposium on Quality Standards for Natural Waters. ix + 317. University of Michigan, Ann Arbor, Mich. 48104. 1967. $5.00, paper.

The symposium was organized to provide an opportunity for workers in

ALL SCOTT RESEARCH GAS MIXTURES HAVE a GUARANTEED ANALYSIS

...in other words our gases are standard gases.

Your verification of the analysis is eliminated, thus saving time and money. Scott Research gas mixtures are made to order in cylinders containing 10 to 200 cubic feet, 1 to 20 trace or minor components in parts per billion to percent concentrations. The "make" tolerance is ±10% and analysis accuracies vary from ±5% to ±1% of each trace component value depending on your requirements. We purify many gases for special applications, including use as zero gases and as major components of calibration standards. Our pure air with total hydrocarbon content less than 0.1 ppm carbon is an example. At Scott Research we have the necessary experience to help you. For further information, call or write. Remember—all Scott Research gas mixtures, complicated or simple, have a guaranteed analysis.

Write for our new specialty gas catalog.

SCOTT RESEARCH LABORATORIES, Inc.

(215) 249-3526
P.O. Box 66, Dept. E,
Perkasie, Pa. 18944

---

the field to explore, in a university setting, several of the issues involved in the establishment of standards on interstate waters as required in the Water Quality Act of 1965. Topics discussed were stream flow regulation, advanced methods of treatment, requirements for specific water uses, the natural ability of streams to purify themselves, water quality characterization, and the management of pollution sources in the effort to meet standards. Discussion periods have been recorded in the proceedings along with the speeches and summaries.

The Fresh Water of New York State: Its Conservation and Use. Edited by Lauren B. Hitchcock. A symposium. xviii + 255 pages. William C. Brown Book Co., Inc., Dubuque, Iowa. 52001. 1967. $5.00, hard cover.

Transmission of Viruses by the Water Route. Edited by Gerald Berg. A symposium. xviii + 484 pages. Interscience Publishers, New York, N.Y. 10016. 1967. $15.00, hard cover.

High-Energy Batteries. Raymond Jasinski. xv + 313 pages. Plenum Publishing Corp., New York, N. Y. 10011. 1967. $17.50, hard cover.

Industrial Water Pollution Control. W. Wesley Eckenfelder, Jr. vii + 275 pages. McGraw-Hill Book Co., New York, N. Y. 10036. 1966. $14.50, hard cover.

Photochemistry. J. G. Calvert and J. N. Pitts, Jr. xvii + 899 pages. John Wiley & Sons, Inc., New York, N. Y. 10016. 1966. $19.50, hard cover.

Residue Reviews. Vol. 17: Residues of Pesticides and Other Foreign Chemicals in Foods and Feeds. Edited by Francis A. Gunther. vi + 184 pages. Springer-Verlag New York, Inc., New York, N. Y. 10010. 1967. $8.50, hard cover.

The A-B-Seas of Desalting. Office of Saline Water. iii + 24 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1966. 25 cents, paper.

Northern California's Water Industry. J. S. Bain, R. E. Caves, Julius Margolis. xvii + 766 pages. The Johns Hopkins Press, Baltimore, Md. 21218. 1967. $15.00, hard cover.

Specific, simple SO₂ monitoring from Beckman.
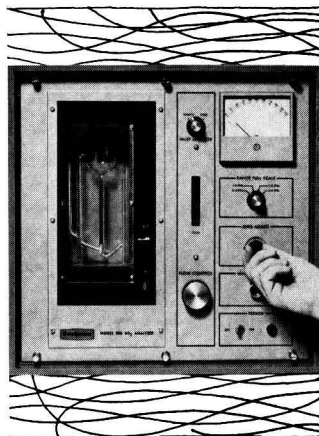
With the new Beckman Model 906 SO_2 Analyzer, you don't have to worry about reagents. Or metering pumps. Or fragile glass contactors. Or complex external sample handling systems. Or many other complex components. **Or** the high maintenance costs usually entailed.

By incorporating the technique of secondary coulometry with a unique end-point detector, and a patented scrubber, which virtually eliminates all interference errors, the analyzer provides rapid, **continuous,** accurate and specific determinations of SO_2 concentrations in ambient air.

SPECIFIC FEATURES. 1. Response time is less than 3 minutes. 2. Zero calibration built in. 3. Panel, wall or bench mountable. 4. Four operating ranges from 0.5 to 4.0 ppm full scale; switch selectable. 5. Linear direct readout, recorder output. Call your Beckman office or write for Data File AP-16-267.

Beckman

INSTRUMENTS, INC.
SCIENTIFIC AND PROCESS INSTRUMENTS DIVISION
FULLERTON, CALIFORNIA • 92634

INTERNATIONAL SUBSIDIARIES: GENEVA; MUNICH; GLENROTHES, SCOTLAND; TOKYO; PARIS; CAPETOWN; LONDON; MEXICO CITY

LETTERS

Lake Erie Again

DEAR SIR:

We all know that if phosphorus could be completely eliminated from the waters of Lake Erie, we would not have the algal problem nor, eventually, oxygen depletion. We feel, however, that the problem is much more complicated and there are other factors involved than simply phosphorus input. I refer to the possible "regeneration" of phosphates from the bottom muds under anaerobic conditions.

We are attempting to measure the fate of the increased phosphorus that occurs under anaerobic conditions after the waters of the lake are mixed. We are also attempting to measure the nutrient requirements of the algae common to Lake Erie to determine what nutrients are limiting and what nutrients are in excess. We have some data to show that the phosphorus level in the central basin of Lake Erie does not vary with plankton density. We also have data that show nitrates disappearing from the surface waters of Lake Erie during plankton blooms. These studies have many ramifications and we do not wish to make our findings known until we have more conclusive evidence to indicate nitrates indeed become limiting before phosphorus. We have found this to be true only for certain forms of algae, namely diatoms and green algae, since certain species of bluegreens can manufacture their own nitrogen.

Let me put our position in this way. We wholeheartedly agree with the steps FWPCA is taking to improve conditions in Lake Erie. We favor maximum treatment for all wastes. We favor maximum phosphorus removal and believe that these steps will have a measurable influence on Lake Erie. Our concern is that these measures will not go far enough to satisfy the environmental requirements of the biota of Lake Erie and are suggesting an increase in research activities to pinpoint problem areas and to answer specific questions concerning the role of various nutrients in the metabolism of Lake Erie.

John F. Carr
Chief, Limnology Program
U. S. Department of the Interior
Ann Arbor, Mich. 48107

MEETING GUIDE

July 3–7
Gordon Research Conference on Environmental Sciences
Air Pollution: The Oxides of Nitrogen
Crystal Inn, Crystal Mountain, Wash.
The aim of the conference is to summarize what is known, discuss research in progress, and suggest further research on the subjects of production, monitoring, effects, and control of the oxides of nitrogen. As usual at Gordon Research Conferences, discussions are informal. Contact Dr. W. George Parks, director, Gordon Research Conferences, University of Rhode Island, Kingston, R.I. 02881, for registration information.

July 5–7
University of Colorado, Colorado State University, and Colorado School of Mines
9th Annual Western Resources Conference
University of Colorado, Boulder, Colo.
In line with the announced theme of Man and the Quality of His Environment, there will be sessions on the quality of the water environment, the quality of the atmosphere, solid wastes as a natural resource, outdoor recreation, urban encroachment and open space, and a community environment case study.

July 5–8
National Society of Professional Engineers
33rd Annual Meeting
Statler-Hilton Hotel, Hartford, Conn.
Among the various committee reports slated for presentation are papers on pollution control and water policy.

July 24–28
Engineering Foundation
Solid Waste Research and Development
University School, Milwaukee, Wis.
Sanitary landfill compaction, gas emanation, composting, incineration techniques, agricultural and farm waste handling, and other aspects of solid waste will be discussed in an informal environment conducive to free exchange of thoughts and ideas. Attendance will be limited to 100, with a registration fee of $140.

August 13–16
Soil Conservation Society of America
22nd Annual Meeting
Hotel Fort Des Moines, Des Moines, Iowa
The theme of the symposium is Soil and America's Future. Sessions will be directed to land management, resource conservation problems, soil erosion, sediment and nitrates in soil and water management, and managing the environment for quality living.

August 23–25
American Society of Civil Engineers (Sanitary Engineering Division)
National Symposium on Estuarine Pollution
Stanford University, Stanford, Calif.
Designed to satisfy the needs of sanitary engineers and scientists concerned with the effects and control of pollution in estuaries, the symposium will cover recent studies on the effects of municipal, industrial, and agricultural pollutants on water quality and aquatic life, as well as the distribution of such pollutants by tidal action, wind, sunlight, temperature, and other physical, chemical, and biological factors. Also planned are discussions on forecasting techniques, model studies, and recent developments in water quality management.

August 28–30
Environmental Engineering Intersociety Board and American Association of Professors of Sanitary Engineering
Second Conference on Environmental and Sanitary Engineering Education
Technological Institute, Northwestern University, Evanston, Ill.
Sessions will focus on the curriculums for environmental engineering students, planning of environmental engineering systems, and the criteria and mechanism for accreditation of programs in environmental engineering, among other topics.

August 29–30
Water Conditioning Association International, Water Conditioning Foundation, and Water Conditioning Research Council
3rd Annual International Water Quality Symposium
Conrad Hilton Hotel, Chicago, Ill.
Water management, economics, supply, treatment, and quality will be examined, with emphasis on health, productivity, and aesthetics.

September 6–9
Society of Mining Engineers of AIME, and Rocky Mountain Minerals Conference
SME Fall Meeting
Las Vegas, Nev.
Technical papers will be presented on solid fuel in pelletizing shaft furnaces, sulfur recovery from coal and flue gases, methane monitoring in coal mines, and acid mine drainage, among other topics.

September 10–15
American Chemical Society
154th National Meeting
Chicago, Ill.
The Division of Water, Air, and Waste Chemistry will present, in joint efforts with other divisions, discussions of scientific information resources for the water researcher; water resources; and adsorption from aqueous solutions. Other programs of interest planned are **Foam Fractionation** by the Division of Industrial and Engineering Chemistry and **Microbial Waste Treatment** by the Division of Microbial Chemistry and Technology.

September 11–14
Instrument Society of America
22nd Annual International Instrument-Automation Conference
Chicago, Ill.
Concurrent with the conference are symposia on data handling and computation, measurement standards, and physical and mechanical measurement instrumentation. The conference will highlight the areas of automation, biomedicine, and food.

September 12–14
Polytechnic Institute of Brooklyn and Naval Applied Science Laboratory
Materials–Key to Effective Use of the Sea
Statler-Hilton Hotel, New York, N.Y.
Current research and development programs and materials problems will be emphasized the first day; the behavior of materials in ocean environments will be summarized the second day; and materials technology in the ocean engineering field will be discussed on the third day.

MEETING GUIDE continued

October 2–6
National Institutes of Health

17th Annual Instrument Symposium and
Research Equipment Exhibit

National Institutes of Health,
Bethesda, Md.

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

October 8–13 and 15–18
Water Pollution Control Federation

40th Annual Conference

Hotel Americana, New York, N.Y.
(Oct. 8–13)

Puerto Rico Sheraton Hotel, San Juan,
Puerto Rico (Oct. 15–18)

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

October 9–12
**Association of Official Analytical
Chemists**

81st Annual Meeting

Marriott Motor Hotel, Washington,
D.C.

Methods, instrumentation, and tech-
niques for analysis of feeds, fertilizers,
pesticides, food additives, hazardous
substances, and other materials, will
be discussed. There will be a special
symposium on drugs.

November 6–8
**American Water Resources
Association**

National Symposium on Ground Water
Hydrology

Mark Hopkins Hotel, San Francisco,
Calif.

The symposium will include sessions on
occurrence of ground water in different
geologic environments; ground water
movement and well hydraulics; sea water
intrusion, artificial recharge, and surface
water-ground water relationships; and
model and radio-isotope techniques in
ground water investigations.

PROFESSIONAL CONSULTING SERVICES

Like to Write?

We are looking for a chemist or chemical engineer interested in writing and reporting on environmental science and technology and on related and interacting legislative, legal, economic, and social developments.

The American Chemical Society's flourishing new publication ENVIRONMENTAL SCIENCE AND TECHNOLOGY offers a challenging writing position in Washington, D.C., to a chemically-trained person with two or more years of professional experience, a desire to write, and a strong interest in the quality of our environment.

ENVIRONMENTAL
Science & Technology

WRITE TO:
RODNEY N. HADER
AMERICAN CHEMICAL
SOCIETY PUBLICATIONS
1155 SIXTEENTH STREET, N.W.
WASHINGTON, D.C. 20036

INDEX TO ADVERTISERS IN THIS ISSUE

▼ ▼ ▼

compare
us WITH OTHER MANUFACTURERS OF AIR POLLUTION CONTROL EQUIPMENT

☐ electrical precipitators
☐ centrifugal collectors
☐ wet scrubbers
☐ catalytic incinerators
☐ thermal incinerators
☐ fabric filters
☐ adsorption systems
☐ dust level indicators

☐ source testing
☐ heat exchangers
☐ stack gas and emission analysis (both particulates and gases)
☐ product and energy recovery studies
☐ design, fabrication, field start-up
☐ trouble-shooting
☐ planning and equipment modernization services

You'll find that from UOP you get the best, most efficient and economical job . . . with complete air correction service, as well. Check us out today. UOP Air Correction Div., Universal Oil Products Company, Greenwich, Connecticut 06830. The company where environmental engineering is important.