# ENVIRONMENTAL Science & Technology

*Emphasizing*
*Water,*
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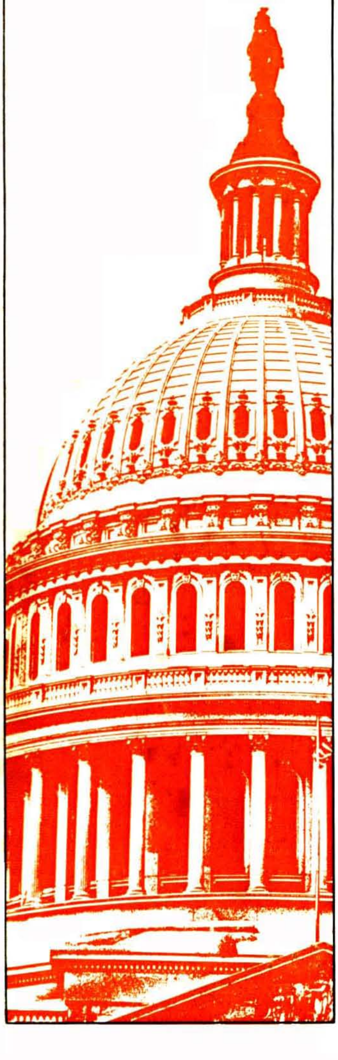
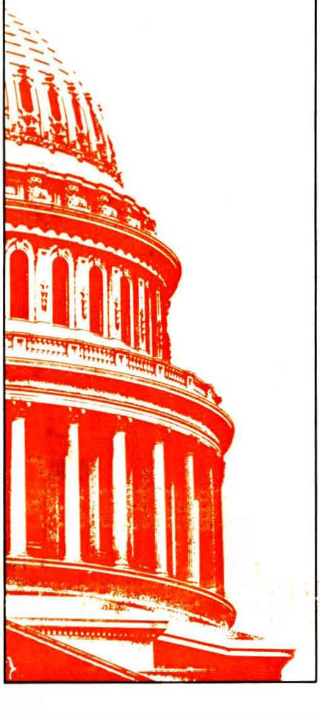
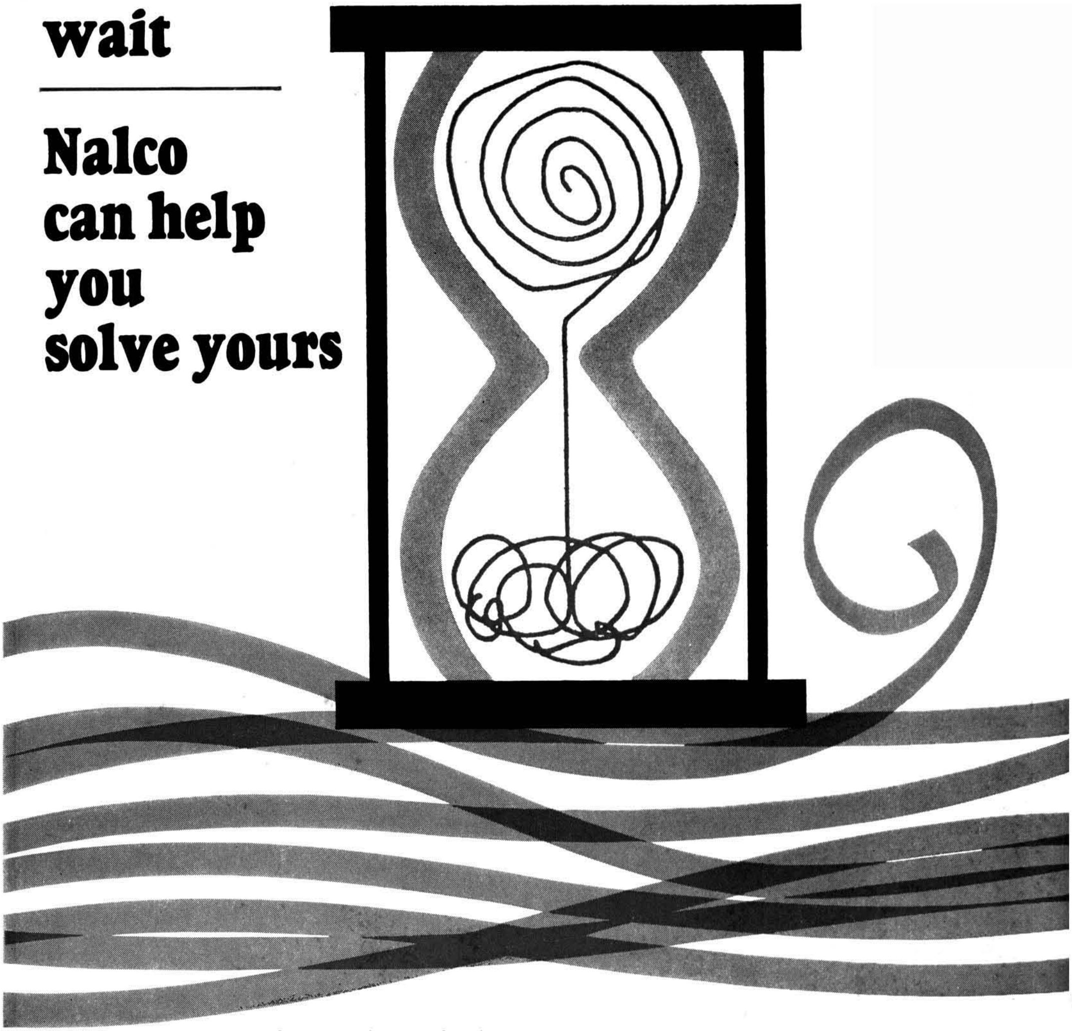
SEPTEMBER 1967







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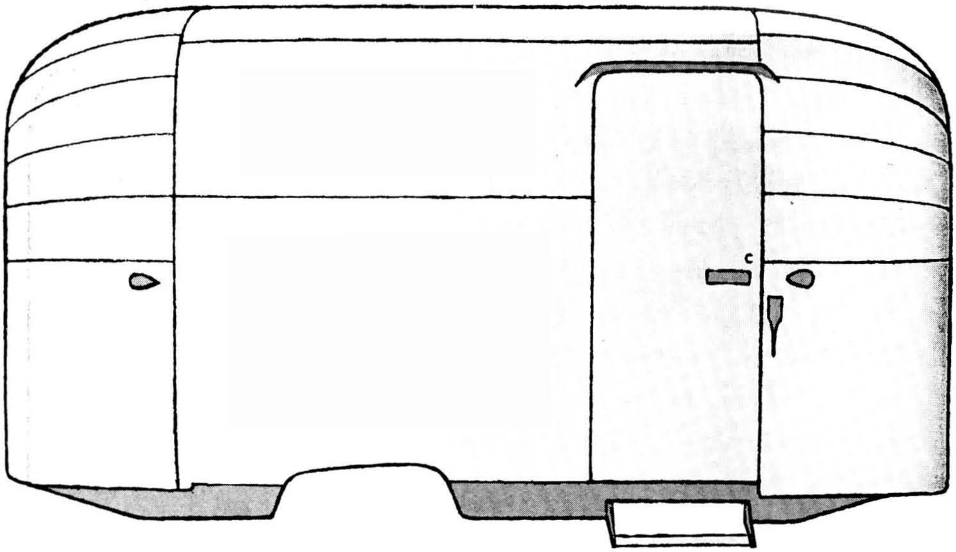

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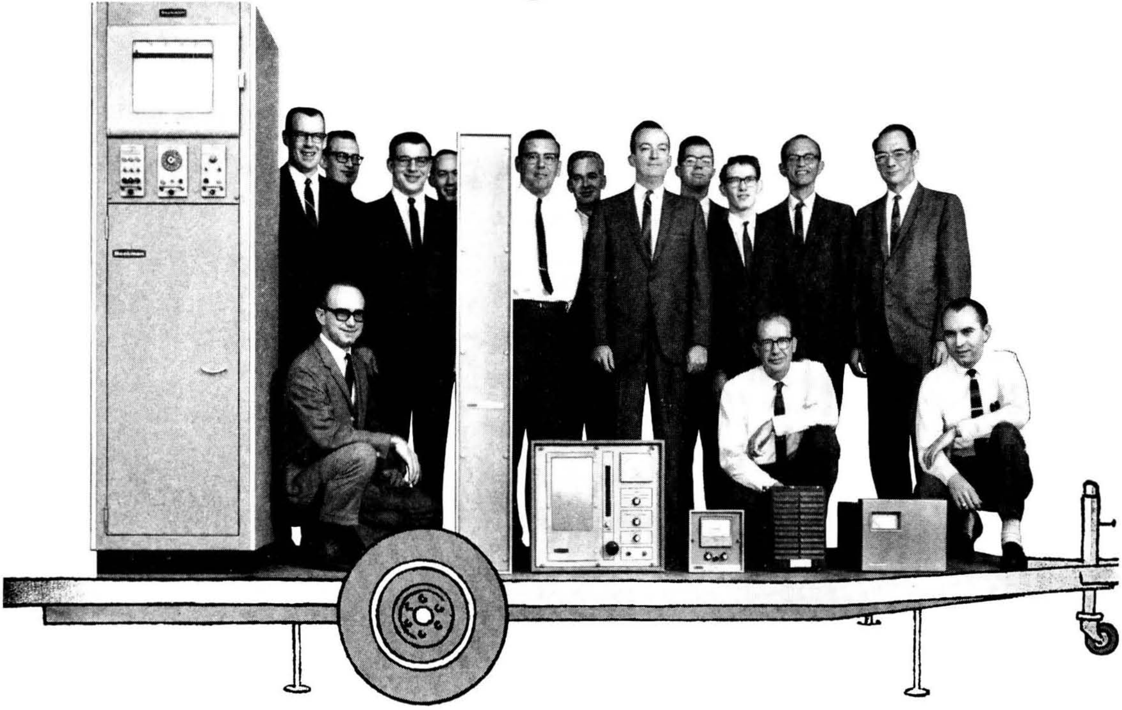

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# ENVIRONMENTAL
## Science & Technology

Volume 1, Number 9
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## Current Research

**Stabilization and determination of traces of silver in waters 717**

**F. K. West, P. W. West, and T. V. Ramakrishna**

Public Health Standards for drinking water include a maximum allowable concentration of 0.05 mg./l. of silver ion. Atomic absorption spectroscopy, a new analytical procedure, readily detects and quantitatively determines silver ion in the 0.01- to 1.0-mg./l. range. Measurements are made on silver dithizonate complexes after they have been isolated and concentrated into ethyl propionate.

**Determination of calcium in natural water by atomic absorption spectrophotometry 721**

**E. M. Bentley and G. F. Lee**

Stringent pH control provides for quick, accurate, and precise analysis of calcium in natural waters. In the pH range of 1.8 to 3.8, correct analyses are obtainable, but outside this pH range the calcium response in atomic absorption analyses is decreased and leads to low values. In addition, the pH dependence of the calcium response is eliminated by adding EDTA to a level that is 50% of that required to titrate the hardness of the water or by adding sufficient lanthanum to make a 1% solution.

**Geochemistry of some Tertiary and Cretaceous age oil-bearing formation waters 725**

**A. G. Collins**

Oil-bearing formation waters can be categorized by concentration differences of ions such as sodium, potassium, calcium, magnesium, chloride, bromide, iodide, bicarbonate, and sulfate. The concentration of bromide ion serves to distinguish Tertiary age waters (low bromide concentration) from Cretaceous age waters (relatively high bromide concentration). Additional correlations were found among several other ions and for some ions and their environments.

**Odorous compounds in natural waters. Some sulfur compounds associated with blue-green algae 731**

**D. Jenkins, L. L. Medsker, and J. F. Thomas**

Malodors and off-tastes in stored surface water supplies may be caused by odorous organic sulfur-containing compounds produced, most probably, by bacterial putrefaction of blue-green algal cells. Methyl mercaptan, dimethyl sulfide, isobutyl mercaptan, and *n*-butyl mercaptan were found, through the use of a gas chromatographic technique, in decaying algal cultures and in reservoir waters containing algal blooms. The rapid rate of atmospheric oxidation and the high volatility of these compounds, however, will probably prevent their becoming a serious taste and odor problem, since they should be easily removed by aeration. The odor of dimethyl sulfide at low concentrations strongly resembles the fishy odor commonly associated with amines such as methylamine and ethylamine.

**Nitrate and other water pollutants under field and feedlots 736**

**B. A. Stewart, F. G. Viets, Jr., G. L. Hutchinson, and W. D. Kemper**

Agricultural fields contribute significantly to ground water pollution because of fertilizers and wastes from feeding operations. In the South Platte valley of Colorado (the test area) the amount of nitrate moving through soil profiles toward ground water varies widely with land use, in the following order: alfalfa fields < native grassland < cultivated dryland < irrigated fields not in alfalfa < feedlots. Ground water samples under feedlots frequently contained ammonium (or a compound releasing ammonia), organic carbon, and had a very offensive odor.

**Atrazine losses from fallow land caused by runoff and erosion 740**

**A. W. White, A. P. Barnett, B. G. Wright, and J. H. Holladay**

Herbicides carried by runoff and erosion from cultivated agricultural lands can be a significant source of water pollution. Atrazine, representative of the herbicides often used on 22 million acres of agricultural land in the Southern Piedmont land resource area, is transported in small but significant amounts in washoff from field plots of Cecil sandy loam. At recommended application rates of this herbicide (3 lb./acre) and under field and rainfall situations most likely to be encountered, atrazine losses in washoff from soils and slopes similar to those of this study will probably occur in amounts of less than 0.1 lb./acre in the first storm after the herbicide application. Losses in subsequent storms should be progressively less.

**Determination of Radiostrontium in Food and Other Environmental Samples 745**

**C. R. Porter, B. Kahn, M. W. Carter, G. L. Rehnberg, and E. W. Pepper**

Hazardous fission products in environmental samples receive quantitative surveillance. In accordance with levels established by the Federal Radiation Council, strontium-90 at the 20-picocurie level and strontium-89 at the 200-picocurie level in food samples are counted after ion exchange separation of the radioactive strontium from other alkaline earths employing an EDTA solution.

## Communication

**Ammonia in auto exhaust 751**

**J. H. Harkins and S. W. Nicksic**

Motor vehicles probably account for as much as 10% of the ammonia in the atmosphere. Concentration levels of 0.2 p.p.m. of ammonia are found in the atmosphere of urban communities, with an average level of 0.02 p.p.m. From the trapped condensate of engine exhaust, concentration levels of ammonia ranged from 1 p.p.m. at idle to 6 p.p.m. at 50 m.p.h. and averaged 2.2 p.p.m. over the entire traffic cycle. The presence of detergent additives or antiknock compounds in the fuel did not affect the level of ammonia in the exhaust.

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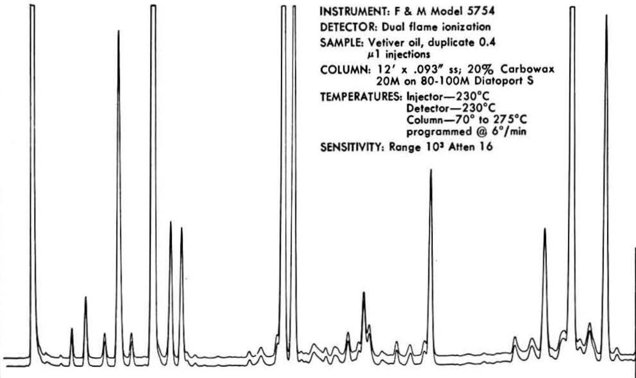
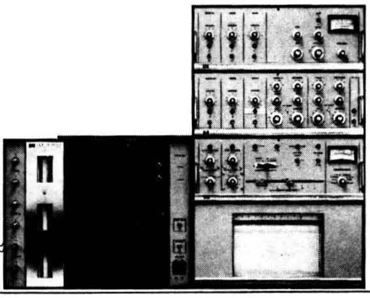


INSTRUMENT: F & M Model 5754
DETECTOR: Dual flame ionization
SAMPLE: Vetiver oil, duplicate 0.4 μl injections
COLUMN: 12′ x .093″ ss; 20% Carbowax 20M on 80-100M Diatoport S
TEMPERATURES: Injector—230°C
Detector—230°C
Column—70° to 275°C programmed @ 6°/min
SENSITIVITY: Range $10^3$ Atten 16



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# EDITORIAL

## Society sometimes speaks with cautious tongue

The several sectors of our society must seek ways to work together yet remain independent, to achieve a wholesome environment

The act of communication requires a sender, a message, and a receiver. One measure of the effectiveness of communication is the degree of fidelity between the message sent and the message received. When green is the message sent but red is the message perceived, there is a sort of communication, albeit faulty.

Another measure of the effectiveness of communication is the kind and extent of the action the message induces in the receiver. Again, if the message is green for go but the action generated is stop, then it hardly matters whether the message is really perceived as green or red or brown. The effective action is stop.

When the message from the public is green, connoting an earnest desire to see an improved, healthful, pleasant environment, there is no communication if the polluters and the legislative controllers read some other color and fail to take effective action to improve the environment.

Dr. Donald F. Hornig, Director of the Office of Science and Technology, points out (this issue, page 709) that the pace of change today leads to dramatic environmental changes in a decade rather than a century. But, he notes, problems of today are not necessarily different in kind from those of 100 or even 1000 years ago. "What is new is the scale, variety, and speed of change, both in man's physical and social environment," he says. He comments further that because technological change is a national necessity in the modern world, we are now unwilling to pay the price of technological stagnation.

Yet, it does seem also that we are often unwilling to pay the full price of technological advancement. We, as individuals, contribute heavily to pollution; en masse, we have wreaked a kind of havoc on the environment. The businessman also detracts through his frequent indifference or his rationalization that doing something about the problem would place his product out of the financial reach of his customers. And legislators often are loath to act for fear of alienating influential groups or of disrupting the economy.

The cycle seems complete. The three concerned sectors of our society are reluctant to admit to their culpability, reluctant to face up to the kind of fiscal responsibility required to meet the price of the technology they demand. Each sector gives lip service to the concept of a wholesome environment, but prefers to leave to the others the reality of achieving it.

Perhaps, then, the real message that the three sectors are sending to one another, and to themselves, is yellow for caution. Perhaps, indeed, there is a fair level of communication among the groups as they seek progress through an infinite number of tiny steps.

Nonetheless, if the caution light means inaction, neglect, or indifference, then the message needs bolstering. Otherwise, the cynics among us may perceive the yellow message as cowardice—an unwillingness on society's part to face up to its responsibilities in preserving or rehabilitating the environment.

Society is simply at another of the myriad crossroads it meets along the evolutionary pathway. The traffic signal at the environmental quality crossroad must be powerful enough to be read through a smog of indifference, special pleading, lack of candor, and unawareness. Each color in the traffic signal has its proper function, the net effect of which is to create some order in a dynamic system without destroying the system's vitality. Any one of the colors, inoperative, out of cycle, or in the wrong proportion, can create chaos.

Melvin J. Josephs

# LETTERS

### California redoubles its efforts

DEAR SIR:

I have just finished reading the article, "California's Auto Smog Cauldron Continues to Bubble," in the July (page 544) issue of your publication. It is an accurate and comprehensive review of the situation as it existed in California at the time it was written.

Several things have happened since the article that give us more confidence than ever in our program.

For one thing, automobile manufacturers universally have agreed to improve their systems and better quality control at their parts plants and assembly lines to assure motorists of even better exhaust emission controls for 1968 models. We have every confidence that past performance will be exceeded in the years ahead.

As for present standards not keeping pace with population growth or being unrealistic in the light of present requirements, we can point to the fact that in two more model years California's exhaust emission standards drop to 180 p.p.m. for hydrocarbons and 1.0% for carbon monoxide. Under the proposed Federal Air Quality Act, California may continue its own certification program for control systems and impose stricter standards than those set forth in Federal regulations.

Second, the State Legislature has just passed the Mulford-Carrell Act for creation of an Air Resources Board. This Board would absorb functions of the Motor Vehicle Pollution Control Board, as well as become involved in stationary source control. We believe it is a strong measure because it does permit the State to step in with civil proceedings when and if a local district fails to act. The State, under the Bill, has the authority to monitor the air and to set Statewide air quality standards. We are happy to enclose a brief summary of the bill's provisions.

Far from relaxing its efforts in the air pollution field, California is redoubling them and again displaying the leadership that has become the model for other air pollution control programs throughout the world.

Credit must go to our people and to our far-sighted Legislature who are determined to rid this beautiful State of such an ugly blight.

Thank you for your interest in our program and for excellent coverage.

Eric P. Grant

*Executive Officer*
*Motor Vehicle Pollution Control Board*
*Los Angeles, Calif. 90013*

### Mulford-Carrell Act highlights

1. Creates a State Air Resources Board to coordinate administration, research, and air conservation activities within the State.
2. Transfers to the Board all personnel, equipment, etc., of the Motor Vehicle Pollution Control Board and Vehicle Pollution Laboratory.
3. Specifies the following duties to be performed by the new Board:
   A. Divide the State into air basins by January 1, 1969.
   B. Adopt ambient air quality standards for each basin.
   C. Assume total responsibility for emissions from motor vehicles.
   D. Adopt emission standards for all sources of air pollution and enforce them if necessary, if, after public hearing and investigation, the Board finds that local authority has not taken reasonable action.
   E. Conduct studies, inventory sources of air pollution, monitor air pollutants, and evaluate the effects of air pollution.
   F. Coordinate and collect research data on air pollution and encourage a cooperative State effort.
   G. Review all rules and regulations of local and regional authority, to assure that reasonable provision is made to control emissions and to achieve the air quality standards established by the State.
4. Permits local or regional authority to adopt standards, rules and regulations more restrictive than those adopted by the State.
5. Provides that all existing rules and regulations, standards, etc., established by existing State authorities shall continue to be effective.
6. Requires, with certain exceptions, that the State Board enforce its standards, rules, and regulations if local or regional authority does not comply within 30 days of a directive from the Board:
   A. When it has been determined that its standards are not being complied with;
   B. When local authority's standards are not being complied with or are inadequate; or
   C. When there is not a satisfactory reply from the local authority to the Board of a reasonable intent to control air pollution.
7. Vests in the Board power to take any appropriate legal action to carry out its responsibilities, including any an Air Pollution Control District could take.
8. Makes violations of Board's standards, rules, and regulations a misdemeanor.
9. If signed by the Governor, the Act becomes effective on or about November 8, 1967.

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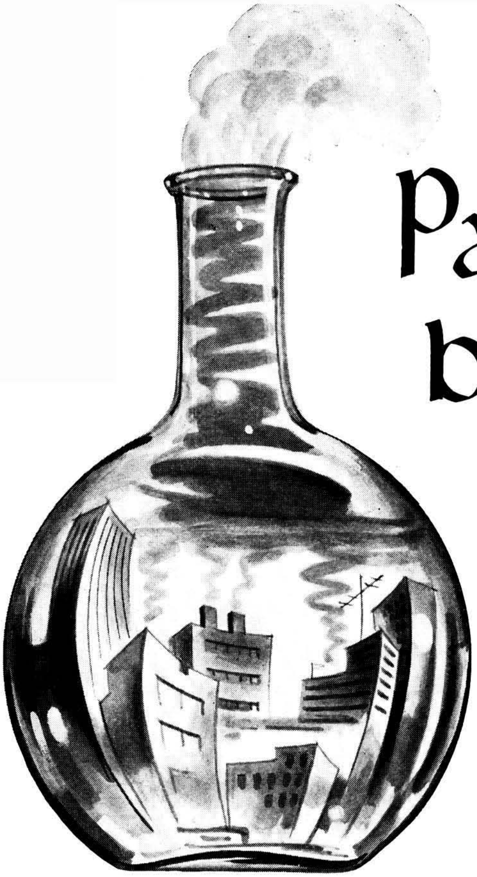
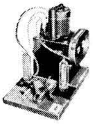
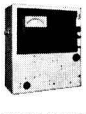
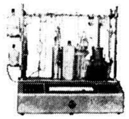
### New ES&T Staff Member Appointed

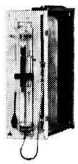
**Stanton S. Miller** has joined the staff of ES&T as an assistant editor. Mr. Miller will devote his efforts to writing and editing material for the staff-generated portions of ES&T and reporting on various meetings, symposiums, and other items of interest to environmental specialists. Mr. Miller comes to ES&T from Syntex (Palo Alto, Calif.) where he had worked since 1965 as a patent chemist. Previously (1960–65), Mr. Miller was on the staff of the Johns Hopkins Applied Physics Lab (Silver Spring, Md.) as an information specialist, and with the U. S. Naval Propellant Plant (Indian Head, Md.) as an organic chemist (1957–60). From 1953–54, he worked with Rohm & Haas as a synthetic organic chemist. Mr. Miller holds his B.S. (1953) in chemistry and M.S. (1961) in organic chemistry from the University of Maryland.

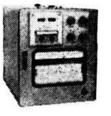




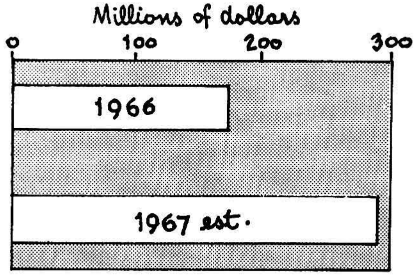








# ENVIRONMENTAL CURRENTS



An NICB survey of 392 companies reveals they plan a markedly increased investment in pollution control equipment this year

## Capital Spending for Pollution Abatement

In 1967 U. S. industry expects to up its spending for pollution abatement equipment by almost 70%. A National Industrial Conference Board survey of 392 companies indicates spending will increase from last year's $171 million to a predicted $291 million this year. Of all industrial categories, only transportation equipment (excluding motor vehicles) will probably show a decrease. Still, pollution expenditures averaged only 1.7% of total capital budget for 1966, ranging from 3.76% in primary nonferrous metals to 0.18% in rubber products. NICB figures indicate that company size is apparently of little significance in determining the extent of a company's expenditures. With the exception of smaller companies (assets of $10 to $25 million and pollution at a rate of 0.5%), all groups averaged between 1–2%. Investment for abatement equipment in 1966 was about evenly split between air and water control; durable goods producers allocate more of their funds to air, while the reverse is true for nondurable goods producers. However, companies reporting to NICB expect to cut their appropriations by about 10% in 1967, with cutbacks coming primarily from the durable goods industries. Many companies feel their expenditures during the next few years will be heavily influenced by new legislation, and most of them see more vigorous legislation coming.

## Predicting Floods via Satellite

A fast, reliable operational system of reporting potential flood conditions is the aim of an experiment the Weather Bureau is carrying out with the National Aeronautics and Space Administration's ATS-1, the synchronous satellite over the Pacific. Three unattended stations (in Arkansas, Oregon, and California) automatically record river levels and accumulated precipitation every 15 minutes and send measurements to the satellite upon demand. The information is relayed to Weather Bureau hydrologists responsible for issuing public flood warnings. But the Weather Bureau is not the only agency exploring the use of satellites to acquire hydrologic data. The Geological Survey's Earth Resources Observation Satellite (EROS), planned for operation in 1970 (ES&T, June, page 460), will study distribution of water, as well as other problems in cartography, geography, geology, and the marine sciences.

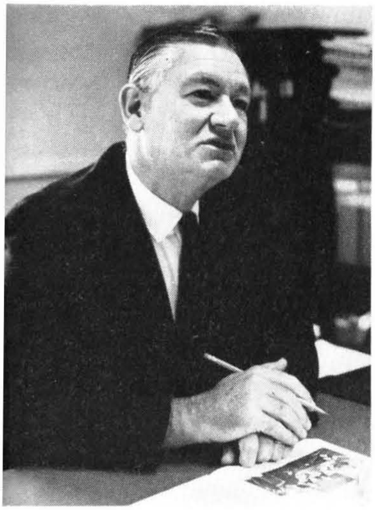
## Pollution—Not for the Cities Alone

Montana, which spreads its 700,000 people over almost 150,000 square miles, is wrestling with two pollution problems: one involves the copper pollution of a trout-rich stream, the other fluoride discharges from a phosphate plant.

The copper pollution is the side effect of the nationwide copper strike, which began on July 15. Ordinarily, water pumped from Anaconda Co.'s mines in Butte goes through a precipitation plant before it is discharged into the Clark Fork of the Columbia River. During the strike, maintenance men have continued to pump the water out; the unions have refused to operate the precipitation plant, since they consider the copper reclaimed in the plant a part of production. Anaconda started adding lime to precipitate the copper, but the river was soon in trouble. One 30-mile section was completely dead. Recalling the six years the river required to recover from pollution resulting from a 1959 strike, the State Fish and Game Department sought and received a restraining order from the courts. Anaconda reopened the precipitator on Aug. 11. A big river with quantities of fresh water being added from many side streams, the Clark Fork quickly bounced back. But to the unions, operation of the precipitator was tantamount to strikebreaking. Under union threat to pull out all maintenance men, Anaconda stopped the precipitator in early September. Instead, it is liming the water twice, then storing it in holding ponds. Fish and Game Department Director Frank H. Dunkle is adopting a wait-and-see attitude: "Anaconda has been very cooperative in our efforts to stop pollution of the river, but if the strike goes on for very long, I don't think the ponds can handle the volumes of water involved. Also, liming gives a copper precipitate that is light and doesn't seem to settle out permanently. Meanwhile, twice daily we are sampling the river at six points along a 70-mile stretch below the waste water input. The Clark Fork has some of the finest brown trout fishing in the United States. We went to court to protect it, and we'll go again if we have to."

The phosphate plant is the subject of the first intrastate air pollution abatement action taken under the Clean Air Act (ES&T, June, page 463). Participants at the conference, which starts off the abatement proceedings, concluded that the air pollution problem "is so serious that, if it were within the power of the conference participants, Rocky Mountain Phosphates, Inc., would be shut down immediately and remain closed until air pollution control measures, operating and maintenance practices have been demonstrated to be adequate to achieve compliance with the Montana Ambient Air Quality Standards." Lacking the power, the participants recommended that the Montana State Board of Health close the phosphate plant until the company indicates how it plans to control the fluoride emissions. The conference recommendations are now in the hands of the Secretary of HEW. Although not required to approve the conference recommendations, the Secretary has gone along with recommendations forwarded by other pollution abatement conferences.

# ENVIRONMENTAL CURRENTS



*Dworsky*
*Technical manpower and*
*technical information*
*singled out*

## New Chief at COWRR

A new chairman has signed in at the Committee on Water Resources Research. He is Dr. Leonard Dworsky, on leave from Cornell University where he is professor of civil engineering and head of the Water Resources Center. From 1946 to 1964 Dworsky worked in the Public Health Service on the federal water pollution control program, where one of his main interests was in integrating pollution control efforts in the over-all water development program. This background will serve him well in COWRR where emphasis is on coordinating the Government's water resources research program (ES&T, May, page 400). The fifth chairman in COWRR's five-year history, Dworsky minimizes the problems of these frequent changes: "My predecessor, Robert Smith, provided a great deal of background to smooth the transition before he returned to the University of Kansas. Many of the other members of the committee have served for a number of years. Working groups in the various areas have continued to function through this transition, and I'm confident our program will move along."

For the year he will spend as COWRR chairman, Dworsky sees two areas coming in for special attention. The first is that of technical manpower: "At its meeting in July the Universities Council on Water Resources, on which I served, posed this problem. UCOWR is concerned about where funds will come from to meet the manpower needs, particularly at the graduate level." The other area Dworsky singles out is technical information, where he sees the start-up of the Water Resources Scientific Information Center having a significant impact.

## Preserving the Habitability of Earth

"Man is becoming a geological and biological agent who through his technology can not only change the world but destroy large parts of it without realizing that he is doing so," says Dr. Roger Revelle of Harvard University and chairman of the U. S. National Committee for the International Biological Program. Fifty nations are participating in the IBP which will initiate and correlate world-wide research efforts directed at an understanding of man's effects on his environment. Dr. Revelle announced five major research programs and 104 individual projects as the U. S. contribution to IBP. The five major research studies include aerobiology, large ecosystems, the Eskimo population, terrestrial life in the Hawaiian Islands, and phenology.

# FWPCA

## An Agency with a Mission

**FWPCA's Weinberger**

*Full range of water quality problems*

Behemoth of those federal agencies supporting water resources research, the Federal Water Pollution Control Administration can fund only those projects that will help fulfill the responsibilities Congress has assigned it

The Federal Water Pollution Control Administration has requested $60 million for research and development in fiscal year 1968. Its budget dwarfs those of the numerous other federal agencies supporting water R&D projects (ES&T, May, page 400). Still, for the laboratory research worker with an idea for a water research project, FWPCA may not be the best agency from which to seek support. One reason: FWPCA is mission-oriented—it can't fund a project on scientific merit alone, but must also consider the objectives of the national program. Another reason: its current emphasis is on demonstration plants.

Dr. Leon W. Weinberger, FWPCA's acting assistant commissioner for research and development, summarizes the agency's R&D objectives this way: "While we emphasize certain areas, we do deal with the full range of water quality problems—from pollution definition and control to water resources management and planning. We also cover the spectrum from laboratory research to full-scale demonstration plants. But for the time being, at least, we will emphasize translating research findings into pilot plants and demonstration plants. A lot of what we know is just not being applied. Such plants are expensive—we estimate that about 50% of our funds for grants and contracts will go to this type of project. We will probably continue to support laboratory research at about the same dollar level as now, or possibly a bit higher. Since our total program is growing, this might mean a drop in the percentage of our funds going into laboratory projects."

The areas FWPCA will emphasize in the coming year are:

- Combined and storm sewers.
- New and improved waste treatment and joint treatment of municipal and industrial wastes.

- Industrial waste pollution control.

Congress authorized $20 million annually for grants and contracts for each category for the next three years. The FY '68 budget includes $10 million for each of these "Section 6" programs.

The combined sewers program, now about a year and a half old, is coming to grips with a knotty problem: thousands of miles of sewers, designed to carry both sewage and storm water, overflow after heavy precipitation. One solution would be to separate them. But that solution could cost $20 billion, and still leave the problem of storm runoff. So FWPCA is considering several alternatives:

- Storing of wastes, usually the storm wastes, since they are easiest to hold. They could be reintroduced into the sewer at off-peak periods. Open lagoons are one way of holding these wastes. Another way is to store the storm wastes under water in inflatable containers. Chicago, with the help of a $1 million grant from FWPCA, will build deep tunnels to temporarily store excess combined sewage flows for return to the sewage treatment plant during off-peak hours. The project will demonstrate reduction of discharges of untreated combined sewage and minimize overloading of the treatment plant. This may prove to be a prototype for an extensive tunnel system for the Chicago Metropolitan area.
- Reducing the amount of storm runoff by such methods as diverting surface runoff; utilizing temporary storage at buildings or in the immediate area by using holding tanks, rooftop storage, backyard storage; storage in the upper portions of drainage areas; and reuse of stored waters for lawn watering, sewer flushing, and similar purposes.
- Reducing the strength of wastes by screening out solids or by in-sewer

## FWPCA's Grants to Date on Advanced Waste Treatment Methods

Grants to January 1967

| Grantee | Amount (dollars) | Title of Project |
|---|---|---|
| City of Chino<br>Chino, Calif. | $ 560,000 | Tertiary activated sludge treatment to reclaim waste for water supply for agricultural and recreational purposes |
| City of Detroit<br>Detroit, Mich. | 299,800 | Pilot-scale study of improved phosphate removal by modified activated sludge process |
| City of San Buenaventura<br>Ventura, Calif. | 90,226 | Integrated activated sludge-biological filter process |
| City of San Jose<br>San Jose, Calif. | 36,100 | Solids and nutrient removal from secondary effluent by foam fractionation |
| County of Nassau<br>Mineola, N.Y. | 700,000 | Advanced waste treatment for water reclamation and reuse by injection |
| Dallas City Water Works<br>Dallas, Tex. | 510,000 | A complete recycle waste water treatment plant |
| East Chicago Sanitary District<br>East Chicago, Ind. | 450,000 | Tertiary treatment of combined storm water, sanitary relief discharges, and sewage treatment plant effluent |
| Eastern Municipal Water District, Hemet, Calif. | 225,000 | Reverse osmosis to remove dissolved solids from renovated waste water used in ground water recharge |
| Government of the District of Washington, D.C. | 293,600 | Full-scale raw waste water flocculation study at the District of Columbia water pollution control plant |
| Government of the District of Washington, D.C. | 300,000 | Use of modified activated sludge treatment to achieve nutrient removal and to provide consistent feed to tertiary treatment system |
| Green Bay Metropolitan Sewerage District<br>Green Bay, Wisc. | 251,250 | Effectiveness and design and operating parameters of four alternative biological treatment processes and modifications for treating combined municipal and industrial waste waters |
| Improvement District No. 1 of Irvine Ranch Water District, Irvine, Calif. | 325,500 | Tertiary sewage treatment for reuse |
| Santee County Water District<br>Santee, Calif. | 800,000 | Renovation of waste effluent for recreational and potable water supply uses |
| South Tahoe Public Utility District, South Lake Tahoe, Calif. | 1,022,000 | Recovery and reuse of lime as a coagulant in tertiary treatment and nitrogen removal from tertiary treated effluent |
| Washington Suburban Sanitary Commission<br>Hyattsville, Md. | 1,650,000 | Design and construction of full-scale tertiary treatment plant |
| **Total, January 1967** | **$7,513,476** | |

Grants, January to September 1967

| Grantee | Amount (dollars) | Title of Project |
|---|---|---|
| Cleveland, Ohio | $ 118,500 | To determine the increased treatment efficiency attainable in a full-scale activated sludge plant through the use of organic polyelectrolytes |
| Dallas, Ore. | 325,104 | To study effectiveness of combined treatment of domestic and industrial wastes by the completely aerobic aeration method |
| Los Angeles County, Calif. | 564,000 | To provide 500,000-gallon-a-day advanced waste treatment and water renovation facility which will provide water for recreation in an arid region |
| Napa-Berryessa Improvement District, Napa, Calif. | 163,220 | To remove waste effluent nutrients and pathogens by intermittent filtration-irrigation and recirculation, and to prevent eutrophication of receiving waters |
| Onondaga County, N.Y. | 289,650 | To demonstrate feasibility of chemical treatment of complex mixtures of industrial wastes in combination with domestic wastes |
| Tualatin, Ore. | 173,100 | To develop a design and operating criteria for a tertiary-type treatment plant, using the extended aeration principle to produce an effluent approaching drinking water quality |
| **Total, Jan.-Sept.** | **$1,633,574** | |
| **Grand total, to date** | **$9,147,050** | |

# FWPCA development and demonstration grants and contracts

## Eligible recipients

### State-related agencies[a]

(a) Research and demonstration projects to develop improved ways of identifying and measuring effects of pollutants on water uses; improved treatment processes for municipal sewage and other water-borne wastes; techniques for ultimate waste disposal; ways to control the quality of water other than by treatment; and new techniques for water quality management and development.

*Grants:* in amounts deemed appropriate
*Contracts:* up to 100% of total proiect cost

(b) Proiects to investigate, plan and construct facilities which would demonstrate:

1) new or improved ways of controlling the discharge of inadequately treated sewage from storm or combined storm-sanitary sewers.
2) Advanced waste treatment and water purification methods (including the temporary use of chemical additives to improve existing treatment processes) and
3) new or improved ways of treating joint (municipal and industrial) wastes.

*Grants:* up to 75% of total project cost. Project must be approved by state water pollution control agency(s)
*Contracts:* up to 100% of total project cost

### Academic institutions or students[b]

(a) Research and demonstration projects to develop improved ways of identifying and measuring effects of pollutants on water uses; improved treatment processes for municipal sewage and other water-borne wastes; techniques for ultimate waste disposal; ways to control the quality of water other than by treatment; and new techniques for water quality management and development.

*Grants:* in amounts deemed appropriate
*Contracts:* up to 100% of total proiect cost

B. Activities to establish or expand training programs related to water pollution control, including payment of stipends to graduate students.

Grants: no matching funds required. However, institutions receiving grants are expected to bear some of the project cost

C. Individual research fellowships in institutions, chosen by individual, and in areas dealing with water pollution control.

Research fellowships: based on type and level of fellowship.

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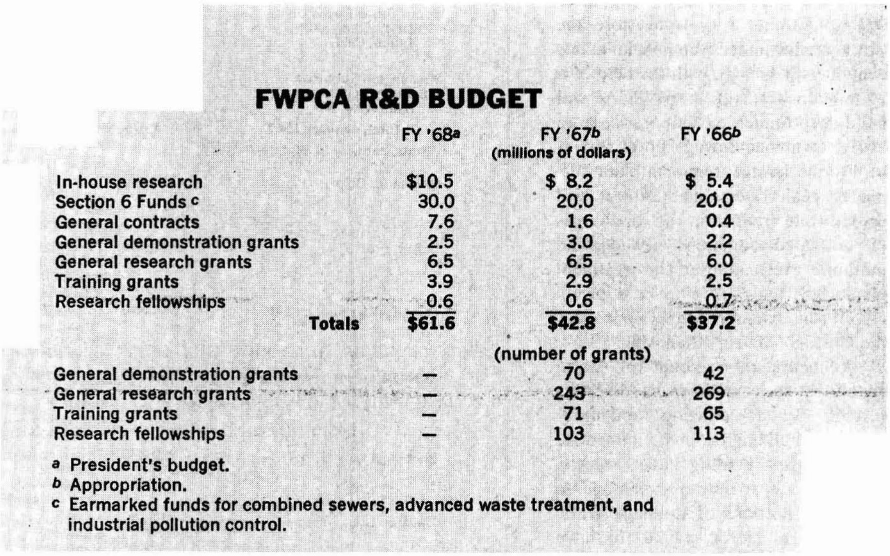
[a] Includes States, municipal, interstate, and intermunicipal agencies.

[b] Includes colleges and universities in the U.S. Also applicable under (a) to nonprofit public and private agencies.

Supportable activities in blue

Type of funding available in black



## FWPCA R&D BUDGET

| | FY '68[a] | FY '67[b] | FY '66[b] |
|---|---|---|---|
| | | (millions of dollars) | |
| In-house research | $10.5 | $ 8.2 | $ 5.4 |
| Section 6 Funds[c] | 30.0 | 20.0 | 20.0 |
| General contracts | 7.6 | 1.6 | 0.4 |
| General demonstration grants | 2.5 | 3.0 | 2.2 |
| General research grants | 6.5 | 6.5 | 6.0 |
| Training grants | 3.9 | 2.9 | 2.5 |
| Research fellowships | 0.6 | 0.6 | 0.7 |
| **Totals** | **$61.6** | **$42.8** | **$37.2** |
| | | (number of grants) | |
| General demonstration grants | — | 70 | 42 |
| General research grants | — | 243 | 269 |
| Training grants | — | 71 | 65 |
| Research fellowships | — | 103 | 113 |

[a] President's budget.
[b] Appropriation.
[c] Earmarked funds for combined sewers, advanced waste treatment, and industrial pollution control.

**Persons, including industries**[c]

1. Research and demonstration projects to reduce and prevent water pollution by industry, including, but not limited to, treatment of industrial waste.

*Grants:* up to 70% of total project cost. Maximum individual grant is $1 million

Results must have industrywide application

2. Same as (a) or (b)

Note: Recipients in this category may participate in (a) or (b) proiects only by cooperating with a state-related agency or academic institution.

*Contracts:* up to 100% of total proiect cost

[c] Includes companies, associations, corporations, individual people, and institutions (profit and nonprofit).

biological or chemical treatment. Treatment methods, as well as control methods, must be capable of handling high-volume, short duration flows occurring at relatively infrequent intervals.

- Increasing the carrying capacity of existing sewers. An example of this approach is evidenced in an FWPCA grant made this year to the Western Co. to study the feasibility of adding polymers to combined sewers to enable them to carry greater quantities of sewage during rains (ES&T, February, page 111).
- Making sewers more efficient by, for example, better external sealing methods to reduce infiltration.

"We have some good ideas working in this area," says Weinberger, who joined the Government's pollution control program in 1963 after 14 years in Case Institute of Technology's civil and sanitary engineering department. "It's still too early to predict how they'll turn out, but, frankly, we could use some new ideas. This is a tough problem that needs imaginative thinking."

The combined sewers grants go principally to cities, which can and do use the technical and manpower resources of industry. FWPCA will finance up to 75% of the R&D costs of a project if the city puts up the rest. Early this year FWPCA granted $8.2 million to cities under the combined sewers program (ES&T, March, page 189). An additional $1.6 million is being used to support contract projects with private companies and organizations. These projects were the first FWPCA has made to such groups. Weinberger expects more such grants and contracts will be made. "The combined sewers program—in fact, all our programs—should be regarded as a challenge to all organizations having research competence. Chemical manufacturers, instrument makers, industry in general, systems analysis people—probably all have expertise that could help us."

In September, four more contracts totaling $1.2 million were awarded for combined sewers projects, along with two demonstration grants totaling $0.9 million.

FWPCA's other major programs, those on advanced waste treatment (processes to be used after primary and secondary treatments) and industrial pollution control, were initiated in November 1966. Early this year the first grants were made under this new authority. Fourteen cities and local government districts received $7.5 million in grants for demonstration and research projects on advanced waste treatment processes; in September, another six grants, totaling $1.6 million, were made. In March, 10 private companies or organizations received funds totaling $2.6 million for research on industrial pollution control projects considered to have potential industrywide applications; 11 grants totaling $2.4 million were made by FWPCA in September.

### General research grants

While these new Section 6 programs were being started, Weinberger was also re-evaluating and revamping the programs FWPCA inherited when it was set up in October 1965 in the Department of Health, Education, and Welfare. These programs, carried on by HEW's Public Health Service, included research grants, training grants, and research fellowships.

In re-evaluating the research grants program, Weinberger emphasizes the dual roles of scientific merit and mission responsibility. "We must first make certain that in supporting a research proposal we will be fulfilling our mission. Then we must assign it a priority as far as the specific objectives of our mission are concerned. This sometimes puts us in the position of turning down good proposals. While complete order is, of course, stifling to research, we must remember what our mission is. And there are other government agencies a researcher can go to—the Office of Water Resources Research and the National Science Foundation, to name just two. From our point of view, we'd like to see scientists think not only in terms of scientific merit but also in terms of solving water pollution, a pressing social problem in our country today."

As part of this re-evaluation, Weinberger has changed FWPCA's reviewing system. Under the system he inherited, proposals were reviewed for scientific merit by a panel of visiting experts. "About three quarters of our research grants in FY '67 went out under this mechanism, as a way of getting us through this early transition period," according to Weinberger.

Instead of visiting panels meeting three or four times annually, Weinberger will use a continuing review system. First, a proposal is reviewed to determine if it fits within the scope of FWPCA's mission and if other administrative details are satisfactory. The proposal is then submitted to scientific or technical review. Such review will be done internally in some cases, externally in others. Finally, it goes to the appropriate division director who assigns it a priority as far as the program is concerned. "Under this system, most applications should have at least a preliminary review in two or three weeks. However, we don't want to commit all our funds because we want to be able to fund late-arriving projects. Accordingly, we will generally make awards every three or four months. In any event, six months would be the absolute maximum an applicant would have to wait for a final answer," Weinberger says.

### Training grants

The training grants program is in for a substantial increase. In FY '67 FWPCA made 71 grants totaling \$2.9 million. The '68 budget allots the program \$3.9 million. Weinberger feels that the entire program, which is aimed at helping meet the professional manpower needs of the expanding water effort, needed reviewing and overhauling. "In the process of this review," Weinberber admits, "some inordinate delays developed in making grants. We've about licked that problem now."

Weinberger sees a training grant as seed money, a way to get a program started. "We make a long-term commitment—up to five years—to give a university time to develop its program, but the commitment is a two-way street," he maintains. "The university must follow the plan it laid out in its

## FWPCA's Grants to Date on Pollution Control Industrial Water

| Grantee | Amount (dollars) | Title of Project |
|---|---|---|
| Grants to January 1967 | | |
| Aerojet-General Corp.<br>Odessa, Tex. | $ 226,500 | Demonstration of industrial water renovation plant at Odessa, Tex. |
| Battelle-Northwest<br>Environmental & Radiological Sciences<br>Richland, Wash. | 180,600 | Removal of ammonia from agricultural run-off by selective ion exchange |
| Beet Sugar Development Foundation<br>Fort Collins, Colo. | 102,000 | Concentration of sugar beet wastes for economic treatment with biological systems |
| Caldwell Lace Leather Co.<br>Auburn, Ky. | 46,340 | Complete treatment of tannery industrial waste for chrome tanning, alum tanning, and vegetable tanning |
| Champion Papers, Inc.<br>Canton, N.C., and<br>Hamilton, Ohio | 700,000 | Improved pollution control by reuse of paper machine process |
| FMC Corp.<br>Santa Clara, Calif. | 29,300 | Cannery waste treatment by the kehr activated sludge process |
| Mead Corp.<br>Chillicothe, Ohio | 299,950 | Determination of effect of influent quality on biological treatments of pulp and paper wastes |
| Minute Maid Co.<br>Leesburg and Auburndale, Fla. | 350,000 | Removal of organics and nutrients from citrus processing plant wastes |
| John Morrell & Co.<br>Ottumwa, Iowa | 489,000 | Demonstration plant using aerobic oxidation channel method for treating packinghouse waste |
| Vahlsing, Inc.<br>Easton, Maine | 196,104 | Demonstration of the feasibility of treatment of potato processing wastes using the activated sludge system; feasibility of combining potato processing waste with sugar beet refining waste; and feasibility of three in-plant closed waste water systems in the sugar beet plant |
| **Total, January 1967** | **$2,619,794** | |
| Grants, January to September 1967 | | |
| Blue Ribbon-Big Y Growers,<br>Yakima, Wash. | $ 374,669 | To evaluate three modifications of the activited sludge process for treatment of fruit cannery wastes |
| Continental Oil Co.,<br>Ponca City, Okla. | 75,886 | To remove iron from mine drainage waters by means of bacterial action |
| French, R. T., Co.<br>Shelley, Idaho | 483,217 | To evaluate modifications of the activated sludge process for full-scale treatment of potato processing wastes |
| Georgia Kraft Co.,<br>Rome, Ga. | 287,700 | To determine the technical and economic feasibility of using cooling towers to reduce pollution of Kraft mill wastes, and to reduce usage in Kraft mills |
| Georgia Kraft Co.,<br>Rome, Ga. | 48,181 | To test treatment of Kraft mill effluent by foam separation |
| Johns-Manville Product Corp.,<br>Manville, N.J. | 82,350 | To demonstrate a completely closed water system for the Fiberglas coating process which would eliminate any waste water discharges |
| Lawrence, A. C., Leather Co.,<br>Peabody, Mass. | 87,215 | To demonstrate on a pilot scale the prima and secondary treatment, by the activated sludge process of mixed chrome tannery waste waters and sanitary sewage |
| North Star Research and Development Institute,<br>Minneapolis, Minn. | 76,585 | To evaluate growing fungi strains for use in biological waste treatment processes applicable to waste streams from the food processing industry |
| Pulp Manufacturers Research League, Inc.,<br>Appleton, Wis. | 483,371 | To demonstrate full-scale in-plant treatment of dilute pumping wastes with a portable reverse osmosis unit |
| Robertson Pulp and Paper Laboratory, North Carolina State University,<br>Raleigh, N.C. | 18,444 | To try to minimize stream pollution by Kraft pulp mills by purification of liquid effluent through stored wood chips normally kept as inventory |
| Whippany Paper Board Co., Inc., Durham, Pa. | 371,455 | To evaluate chemical oxidation with chlorine as a method of treating paper mill process wastes |
| **Total, Jan.-Sept.** | **$2,389,073** | |
| **Grand total, to date** | **$5,008,867** | |

proposal. We have universities coming to us now for a five-year extension. It seems to us that after the initial period, the university should be willing to take on such things as salaries, equipment, and facilities."

Another problem Weinberger faces is the design and aim of the overall program. "We've been working on the training grants program for about a year now, and we are trying to set up a policy that answers such questions as: Should our grants support mostly graduate or undergraduate programs? Are we now supporting enough sanitary engineering departments, for example, and should we be putting our money into sanitary chemistry departments, instead? Universities sometimes resent this—'the Government is trying to tell us what to do,' they say. But Congress and the President ask us for just such guidelines, and we have to set them up."

### Transition period over

Come October, FWPCA will celebrate its second birthday. As far as the agency's R&D is concerned, Weinberger regards these first two years as a period of transition—a period that is now about over. "As a new agency in a new department we faced certain problems. We inherited existing programs that needed coordination and review. We were given new large scale programs that took time to get under way. Our program is growing and evolving in the framework of a larger federal effort in water resources research that is also growing and evolving. But the machinery has been set up now, and we can concentrate on a full scale attack on the tremendous problems of water pollution."

# Impact of Water Quality Standards

Although the cost of achieving adequate pollution control will be high, control is needed and action to achieve it must be continued

Consideration of the economic impact of water pollution control, brought about by the Water Quality Standards Program initiated by the Water Quality Act of 1965, should begin with a description of the nature and the extent of the problem. Water pollution, like other forms of environmental pollution, is a consequence and a reflection of the society in which we live. There are many varied and complex reasons for our present predicament:

- The long time mismanagement of and disregard for natural resources.
- Our ever-growing resources.
- New and expanding industries.
- Continuing shift from rural to urban living.

It is not necessary to dwell on these historical and sociological aspects of the problem. It is only necessary to recognize that our waters are severely polluted. The American people are deeply concerned about pollution of the environment. Hardly a day goes by without every major newspaper in the United States carrying an article concerning pollution of the environment. The American people are voicing demands for more effective programs to control pollution, to combat urban blight, to provide adequate parks and recreation sites, and even to reduce the noise from their city streets. In addition to this concern for quality in the environment, there is widespread recognition of the importance of better water management—of which pollution control is very much a part—to meet growing water needs.

Although our nation has experienced wealth and dynamic progress, we have succeeded economically largely at the expense of our easily available and valuable supplies of water. Unless we remember and recognize that no other natural resource can be developed without this resource, the American economy will be in trouble. This became very meaningful in the northeast part of the country, where the prolonged drought heightened awareness on the part of many industries and communities. The citizens of this country now recognize the need for corrective action. Through our democratic institutions, these needs have been expressed in recent years in a series of unprecedented legislative enactments by the Congress of the United States.

Before reviewing the Federal Government's role, it is first necessary to recognize that pollution control in the United States is a responsibility shared among federal, state, and local levels of government. Basically, this responsibility begins at the local level of government with construction and operation of waste treatment plants and enforcement of local ordinances and rules. The state governments have a primary responsibility for regulating pollution within their boundaries. All of the states conduct regulatory programs and, in some cases, two or more states have joined to form interstate control agencies.

### Government role

The Federal Government's role has been a rapidly evolving one. Despite a long history of federal participation in pollution control, principally in conducting research and investigations, the first comprehensive federal pollution control legislation was not enacted until 1956, less than 11 years ago. Major additions to this legislation followed in 1961, 1965, and 1966. In each case, federal involvement was substantially increased, basically reflecting a national determination to get the job done.

Today, the federal program, as conducted by the Federal Water Pollution Control Administration, includes a comprehensive range of activities such as enforcement, research, training, technical investigations, and provision of financial and technical support to state and local governments and others. In addition, a number of other federal agencies have ancillary responsibilities in this field. Increasing federal participation over the years, however, has called for equal response through increased and more effective action at both the state and local levels. The need to develop new patterns of cooperation among the various levels of government concerned is emerging very clearly.

To combat pollution on a national scale will require the expenditure of billions of dollars over the next decade by local and state governments, as well as by the Federal Government working with the private sector of our economy. Most of the money will probably be spent for construction purposes—to build waste treatment facilities that are long overdue. In addition, substantial sums must be expended for research, for training personnel to meet our severe manpower needs, for better resource management (aimed at preventing water pollution rather than halting it after it has occurred), and, finally, for the necessary steps to enforce the national law.

### Water quality standards

While construction goes on and as research takes place in the laboratories, a larger and potentially more effective development is occurring in this country—the establishment, for

**Albert C. Printz, Jr.**
**Federal Water Pollution Control Administration, Department of the Interior, Chicago, Ill.**

Legislators attack boat pollution of water
A wave of new technology and chemicals is needed
to help solve the mounti
problem effectively

As the battle against water polluti
intensifies, many states are pass
laws prohibiting pleasure boats
other watercraft from dumping
treated
to state waters.
into the act late
resident Johns
a portable

Wells Periled by Chemical

A number of water sources
in Carroll County, Va., face
water pollution threats
as result of a mishap that
spilled 5700 gallons of for-
maldehyde Wednesday nigh
The formaldehyde wa
down the side

York adopted
S. 2182), and its
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ng to set effluent
devices. The

LBJ Works
On Message
To Congre

Associated Press
President Johnson
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in the near futu
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Christian said M
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urned to

Pollution

The President's strong
ought to move Congress to the prompt en
of the Air Quality Act of 1967 for which
This six-point program will launch a more
sive Federal intervention in this area thar
would have thought possible a few years
clear that the Nation, having only barely
edged the existence of a problem
now finds that it has
ready

The Balance of Nature
Is Jolted by the Wreck
Of Tanker Off Britain
• • •
Oil and Detergents in Area
Are Killing Fish and Birds;

The tanker Torrey Canyon was bomb
with tons of high explosives by British plane
which then dropped incendiary bombs in
attempt to burn its leaking oil cargo from th
The planes planned to continue droppin
diaries today to keep the oil burning. O
the U.S.-owned tanker, which ran agroun
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parable the $16.5 million da
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61,000-ton, 974-foot long ship
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Home Water Purifier Bu
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By NORMAN
Staff Reporter of TH
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D.C. Scores
Purity Plan
For Potomac

posed making the Potomac
River a national model of con-
servation, with water clea
enough for swimm

Reservoir Syste
omac
Urged to End Water Shortages Here

By Jim Hoagland
Washington Post Staff Writer

Abel Wolman is a slight, scholarly water expert who distrusts and dislikes the Poto-
cause it is "a very er-

man warned, because of the area's mounting population. A system of reservoirs is needed on the river north of Washington to store the excess water
downstream dur-

with a 180-billion gallon reservoir. The proposal was shelved because of protests from citizens, the Interior Department and COG.

"I want a thorou
sion of this,"

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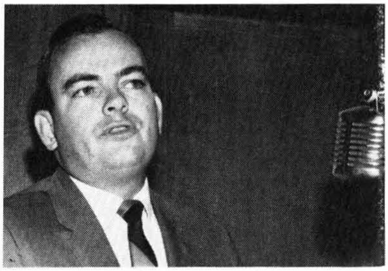
36,330,000 con
o design, supervise construction and help
quip an electric power and water desaliniza-
on plant at Jidda, Saudi Arabia.
All
contract will be paid
warded a
Department

fresh water daily in addition to 50 megawatts
5 million gallons of
of electric power.
The Interior Department's Office of Saline Water will pay Burns & Roe $30,000 to adapt for the proposed Jidda facility a universal de-
sign for a 2.5-million-gallon-a-day des



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the first time in our history, of standards to ensure the quality of our water. The setting of such standards was mandated by Congress under the provisions of national legislation passed in 1965. One of the flaws in the federal regulatory authorization which existed until then was that action could only be taken after the fact and after the damage by pollution had occurred. Setting of water quality standards, as required by the 1965 legislation, provides the means of preventing pollution before it occurs, because the standards specify the water uses to be protected and the water quality necessary to provide for those uses.

The establishment of water quality standards on a national scale is an unprecedented approach to turning back the damaging tide of many wasted years. A number of states had earlier established water quality standards under state law, but, generally, these standards had not proved effective in regulating pollution. This was primarily because the standards were either so low as virtually to constitute a license to continue pollution, or they were not vigorously enforced. The objective of the present Water Quality Standards Program is to enhance the quality of America's waters by upgrading polluted waters and preserving high quality waters where they already exist. The standards seek to achieve this objective through a three-pronged attack. First, the state determines through a series of public hearings, the use or uses of the interstate body of water. Second, to meet the determined use, necessary criteria of water quality are decided upon. And, finally, a plan is devised to assure timely achievement of the selected goals.

In accordance with the provisions of the law, each of the states submitted water quality standards to the Secretary of the Interior for review and approval. Many of these have already been approved and, by virtue of this approval, are now federal as well as state standards. The law provides that the standards should be enforced by the states; should the states default in this responsibility, then the Federal Government will enforce them.

### Guidelines

As a prelude to the standards-establishing process, the Federal Government provided the states with broad guidelines for formulating their standards. For example, it was stated that:

- None would be acceptable which permitted water quality to be further degraded.
- No stream was to be used solely as a waste carrier.
- The criteria must be acceptable to every vested interest in water use.
- No standard would be approved unless consistency and compatibility existed among the standards of a particular river basin.

Although the states have done an outstanding job, in almost every instance where the standards have now been approved by the Secretary, the states were required to go back and make adjustments in the standards before approval could be given.

The states were instructed that good standards which are achievable are better than ideal standards which are not. We did not strive for the highest possible standards, but more realistically, for the highest standards possible.

### Implementation

One of the most important aspects of the Water Quality Standards Program is the development of a satisfactory plan of implementation or a method by which the water quality criteria would be met within a reasonable period of time. In order to prepare such a program, the states were again given guidelines concerning this aspect of the standards-setting process. The plans submitted by the states were to include time schedules for achieving the water quality objectives. These time schedules include target dates by which each known waste discharger must provide adequate treatment. The degree of treatment required will depend, of course, on the quality of the water specified by the standards. The time schedules, as established, were to provide generally for abatement of all existing conventional municipal and industrial pollution within a five-year period. Programs for more complicated problems, such as combined sewer overflows, might reasonably be scheduled over a post-five-year period. The measures to be used by the state pollution control agencies to ensure compliance are also specified in the enforcement plans of the standards.

### Abbreviated procedure

In establishing the Water Quality Standards Program, it was not the intention of Congress that the water quality standards be mere promises of good intentions on the part of the states. They are to be powerful weapons in the war against water pollution because they are to be effectively enforced. When they are violated, the Secretary of the Interior can proceed immediately with a suit against polluters. The usual conference and hearing stages of enforcement will be omitted.

Because of this abbreviated procedure, the enforcement of pollution abatement should be a good deal quicker than it has been in the past. This does not mean, however, that we have in any way discarded our preference for cooperative action. We believe now, as always, that cooperative action taken in agreement with state and local authorities is by far the best way of operating and is likely to be more earnest, more effective, and cheaper for all concerned than action enforced by court orders.

### Costly program

As economists, you are probably asking how much cleanup through the Water Quality Standards Program will cost. The program will be costly; however, this has been recognized by the people. If Congress had given consideration only to costs, such a program might never have evolved. At the present time, there are no satisfactory estimates for the total cost of pollution control. All are deficient in some way or another, usually in regard to such aspects as land drainage effects, bottom deposits, and the varied industrial waste flows.

A most popular figure is 20 billion dollars by 1972, but that figure refers only to the cost of building municipal sewage treatment plants. It is not a firm figure, though much more is known about this aspect of the problem than any other. The estimate is developed from an inventory of municipal facilities which reflects a backlog of needs, an obsolescence factor, and future growth. The infirmity of the figure is due to its heavy reliance on past concepts of treatment and operation, and on uncertainty in regard to the extent to which municipalities will be able to provide treatment service for the industrial operations not now served.

Congress has expressed dissatisfaction with the estimates and has required the Secretary of the Interior to develop reliable figures on the cost of treating industrial and other wastes as well as municipal wastes. This request by Congress is written into the Federal Water Pollution Control Act as Section 16.1(a): "In order to provide the basis for evaluating programs authorized by this Act, the development of new programs, and to furnish the Congress with the information necessary for authorization of appropriations for fiscal years beginning after June 30, 1968, the Secretary, in cooperation with State water pollution control agencies and other water pollution control planning agencies, shall make a detailed estimate of the cost of carrying out the provisions of this Act; a comprehensive study of the economic impact on affected units of government of the cost of installation of treatment facilities; and a comprehensive analysis of the national requirements for and the cost of treating municipal, industrial, and other effluent to attain such water quality standards as established pursuant to this Act or applicable State law. The Secretary shall submit such detailed estimate and such comprehensive study of such cost for the five-year period beginning July 1, 1968, to the Congress no later than January 10, 1968, such study to be updated each year thereafter."

This finished report will provide much information, including:

- An estimate of the total magnitude of water pollution problems in terms of significant waste loads and treatment costs.
- The relative contribution to national water pollution problems by municipal, industrial, and other effluent sources.
- The total estimated cost to attain different levels of pollution removal.
- Comparable cost per pollutant quantity removed by major water-using industries, considering the value of the product.
- Possible remedies with associated cost estimates of unquantifiable "other effluent" problems.

### Billion dollar requirement

The figures that we hear, relative to the cost of pollution control and what has been expended over the years, are large. They are large indeed, even from our bureaucratic conception. As an example, U.S. Steel Co. states that it has invested about 200 million dollars on air and water pollution control facilities in the past 15 years, out of a total 5 billion dollars invested in new facilities. For the three-year period 1966–68, its average annual expenditure for these purposes will exceed 600 million dollars. The American Paper Institute has invested over 200 million dollars for waste treatment facilities up to the end of 1965. The institute further estimates that a 1 billion dollar investment is needed to meet the requirements of the future. Whatever the industrial record has been in the past, it has not been good enough, judging by the general condition of the public waters.

### Investment opportunity

This trend toward treatment will continue in the future, but on the other side of the coin there is a different market associated with the water pollution control investments. This market can be characterized very simply, as was done recently (July 10, 1967) in the *National Observer*: "The big business of cleaning air and water—there is a scramble for profits in controlling pollution." The article goes on to state that waste makes profits, and that many corporations have discovered an expanded market for equipment to extract pollution from the air and to scrub it from water. Equipment sales to control air pollution, as one example, have risen an estimated 30% yearly over the past three years. This result is a bull market for stocks in pollution control companies. This boom is likely to grow as various units of government establish and tighten controls on the wastes that industries and municipalities pour into the sky and water. The boom will not be limited strictly to equipment manufacturers. Worthington Corp. officials predict that spending for water pollution control devices will soon average about 160 million dollars annually, about double current rates; but the cost to build the pipelines and facilities to supply and house this equipment will cost another 3 billion dollars yearly.

In conclusion then, it is apparent that the cost of achieving adequate pollution control through water quality standards will be large. There is general dissatisfaction with present estimates, their costs, and their probable distribution among governments and industry; and their impact on the economy, including effects on public borrowing, interest rates, tax levels, prices, and profits. These matters are under study and reports and recommendations will be available to Congress by the first of 1968. In the meantime, control and action must continue; the requirement for studies does not suggest further waiting. It is along these lines that the Federal Water Pollution Control Administration has set its course.

# Water Management

## A rapidly growing market

Suppliers of water treatment chemicals are expanding their lines and making more services available to fill the need of a rapid-growth market

**Bruce M. Putnam, Arthur D. Little, Inc., Cambridge, Mass.**

The cycle of water usage begins at or near its source, where water is treated and put into the transmission and distribution system. In this initial treatment phase, a variety of chemicals may be used to improve the quality of the raw water, and it is this aspect of water management that most people associate with the use of chemicals. And yet, the largest dollar volume and the most profitable sale of chemicals occur elsewhere.

Water for domestic purposes is normally used only once—that is, water enters our homes from the distribution system, is used, and then passes into the waste collection system.

Industrial use of water can be somewhat more complicated. Depending upon the process or the purpose for which the water is to be used, the water may require some form of special pretreatment; it may also be recycled within the plant to recover such values as heat, chemicals, or just the water itself. It is for industrial purposes that the greatest expenditure for water treatment chemicals is now made. Whereas chemical usage for influent water treatment is usually based on fairly well established dosage levels and involves a limited number of essentially basic chemical products, effective treatment of industrial process water often requires chemical formulations developed specifically for single purposes and based upon intimate knowledge of the processes involved.

At some point, water is discharged from a plant when it can no longer perform a useful function or when its rehabilitation to previous quality levels becomes too expensive. Without going into the details of waste treatment, suffice it to say that municipal and plant effluent today is either discharged untreated or receives some combination of primary and secondary treatment which, taken together, may remove approximately 90% of the suspended solids and a somewhat lower percentage of the oxygen demand. Today, waste treatment accounts for the smallest portion of the market for both bulk and specialty chemicals used in water and waste treatment; estimates vary, but are generally in the 10 to 15% range, with about half of the market being taken up by in-process treatment and about 30 to 35% for the treatment of influent water. Water quality and, therefore, the cost of treatment, has been far more important regarding influent and in-process water than waste water.

However, with the ever-increasing pressure brought to bear on industries

**Water and waste water treatment chemicals**

| Type | Growth prospects |
|---|---|
| **Bulk chemicals ($90 million)** | |
| Chlorine | Moderate |
| Alum | |
| Lime | |
| Soda ash | |
| Other | |
| Ferric chloride, ferrous sulfate, acids, clays, potassium permanganate, powdered carbon, and the like | |
| **Specialty chemicals ($165 million)** | |
| Coagulant aids | Excellent |
| Ion exchange resins, zeolites, chelating agents | Good |
| Slimicides, bactericides | Good to excellent |
| Granular carbon | Good to excellent |
| Corrosion inhibitors | Good |
| Other | |
| Antifoamers, silicates, membranes, structural plastics, deodorizers, solvents, and the like | Good |
| **Related technical services ($20 million)** | Excellent |

and municipalities by federal, state, and local governments, greater attention is being paid to more effective control of effluent quality. Under the Water Quality Act of 1965, almost every state submitted water quality criteria as required by July 1 of this year. While not all states have proposed adequate standards, there is every reason to expect that in the relatively near future they will develop standards which are acceptable to the Federal Government.

The major import of this Act is not so much the setting of the stream criteria themselves, but exactly what these criteria imply for the future. The establishment of water quality standards is merely the first step toward effective control of effluent streams so that their discharge will not adversely affect the quality levels of the receiving bodies of water. The implication here is, obviously, that increasing attention will have to be paid to the quality—and therefore, the manner of treatment—of effluent streams, both from municipalities and industry.

The goal of the Federal Government appears to be to achieve the equivalent of secondary treatment of waste streams by 1975. If this is to be accomplished within such a time period—and again I suggest that it may only be an initial step—there is much to be done.

Capital expenditures for water and waste treatment systems are expected to rise from an estimated $3.5 billion in 1965 to something over $7 billion by 1975, and a great deal of this increase in expenditure will be as a result of the construction of new waste treatment facilities. Beyond primary and secondary treatment is the probability of increasingly sophisticated waste treatment methods which, in at least some cases, should result in the production of water of sufficiently high quality to be fit for human consumption.

### The chemical industry

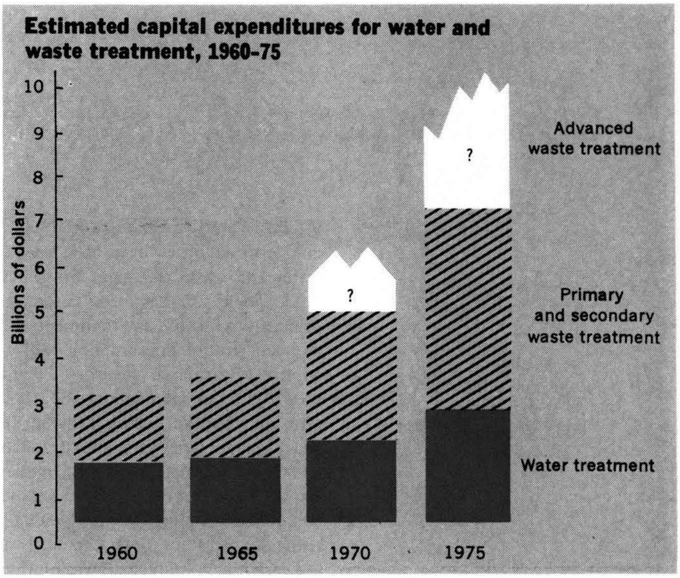
The over-all water and waste treatment industry is one of significant future growth potential. The current estimated market for both bulk and specialty chemicals and related services in the water and waste treatment field is $275 million, broken down into $90 million for bulk chemicals, $165 million for specialty chemicals, and $20 million for related services connected with chemical sales.

Bulk or commodity chemicals, such as alum, lime, chlorine, acids, soda ash, powdered activated carbon, clays, and ferric chloride, have been used in water and waste treatment for a long time. Their use has been associated primarily with influent treatment and, as such, future consumption will be controlled in large measure by the growth of our population and economy and the increasing demand for water-using equipment and products.

To this normal but rather modest growth pattern must be added another component relating to the gradually rising demand for bulk chemicals in industrial and municipal waste water treatment, for essentially the same purposes as in water treatment—coagulation, filtration, pH regulation, and odor control. Another bulk chemical, tonnage oxygen, may well have an attractive future in waste water treatment. The growth prospect for bulk chemicals, as used in water and waste treatment, are at least moderate.

The most attractive opportunities for chemicals lie in the specialty chemical field, which includes products as coagulant aids (primarily the polyelectrolytes), ion exchange resins, slimicides, bactericides, chelating agents, corrosion inhibitors, antifoamers, granular activated carbon, and plastic membranes. One of the most interesting and widely publicized areas involves the use of polyelectrolyes, which to date have been used mainly in combination with inorganic flocculants for influent water treatment. These materials are not yet widely used in municipal water and sewage plants, often because of their high cost—on the order of a dollar per pound or more.

Operators are learning, however, that the high unit cost of polyelectrolyes is often more than offset by their flocculating power. Considerable flexibility is afforded. Depending upon the nature of the stream being treated, it may be more economical to use only a polyelectrolyte or a blend of polymer and inorganic chemicals. With regard


Estimated capital expenditures for water and waste treatment, 1960-75

to efforts in pollution abatement as well as in water treatment, a major factor favoring polyelectrolytes is the fact that these polymers often increase the capacity of existing facilities. This is particularly important with respect to treatment plants faced with peak loads. Also, tailored polyelectrolytes may be developed to treat a variety of specific waste treatment problems, making this an even more specialized area of chemicals.

### Granular activated carbon

For the purposes of this discussion, granular activated carbon (as distinguished from powdered carbon) is classified as a specialty chemical. While granular carbon has been used for an almost infinite variety of purposes, its application in waste treatment has been seriously considered only within the past several years. It may be used either downstream from a secondary treatment plant, or, in the case of the procedure announced by Calgon earlier this year, in conjunction with the use of polyelectrolytes to replace both the primary and secondary steps in sewage treatment. The material has also been used for influent treatment.

In either case, the purpose of the carbon is to remove objectionable taste and odor characteristics and to filter organic materials. An advantage of using granular instead of powdered carbon is that it can be regenerated by burning off the adsorbed impurities; normal carbon losses associated with this regeneration step should amount to 5 to 10% per cycle.

On a long term basis, membrane desalination processes, principally electrodialysis and reverse osmosis, should play an important role in advanced waste treatment. Currently, the two best known membrane types are a modified polystyrene for electrodialysis and a modified cellulose acetate for reverse osmosis. Industrial- and government-sponsored research is pushing ahead in these two fields, and more effective membranes in terms of life, production rate, and extent of dissolved solids removal can be expected. An indication of such effort is the recently announced Permasep process by Du Pont, which involves the principle of reverse osmosis.

Quite obviously, the use of such techniques as reverse osmosis and electrodialysis are applicable not only to advanced waste water treatment but to initial demineralization of poor quality feed water. Many areas in the U.S. have either inadequate quantities of water, poor quality of water, or both conditions. As their need for water increases and as the need for better water quality grows, so will the market for equipment and chemicals to process that water.

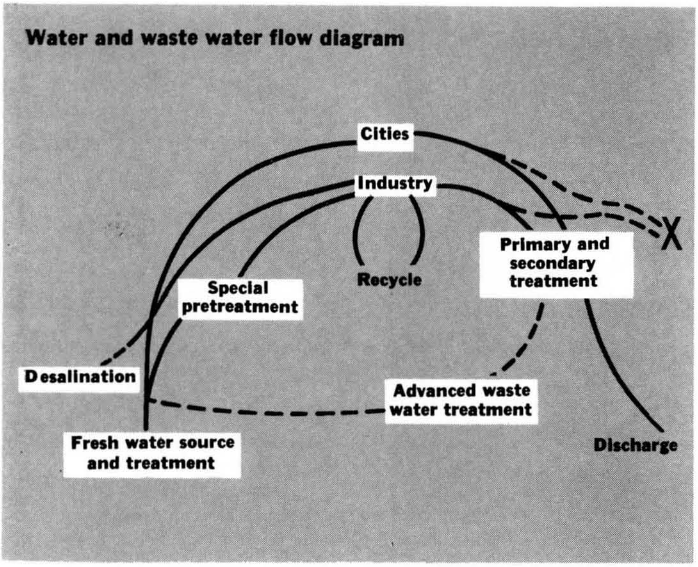
Water quality is not merely a function of total solids content; hardness per se can be and is an important factor in many areas of the country, and there is a significant market for home water softening equipment involving the use of ion exchange resins. This market can be expected to grow quite rapidly also, but will face increasing competition from methods which reduce the total solids content of the water being treated.

The outlook for other specialty chemicals—bactericides, corrosion inhibitors, antifoaming agents, and solvents—is also favorable. The combined factors of industrial growth, increasing water needs, and more stringent pollution abatement requirements will force users of these specialty chemicals to increase their dependence upon them and the services offered in connection with their use.

### Chemical demands

Five factors will be major determinants in affecting future demand for chemicals used in water and waste treatment and in the development of improved chemicals. These are:

**Increased recycle of process water.** Industrial facilities are being forced to



pay stricter attention to their use of in-process water and to devise means of improving or reducing the effluent connected with manufacturing processes. On balance, these developments will mean a larger demand for specialty chemicals used to prevent bacterial and slime growth, to inhibit corrosion, to deoxygenate water, and to reduce solids content.

In-process recovery of chemicals will receive greater attention, and the actual manufacturing processes involved will be carefully scrutinized with an eye toward reducing or eliminating the need for waste water treatment facilities. In some cases, this may actually reduce the demand for waste treatment chemicals via changes in processes.

**Decreasing land availability.** New land for industrial expansion is not cheap, and often in the case of an already established plant simply may not be available. The same is true to a lesser extent with regard to the construction or expansion of municipal water and waste treating facilities. Efforts will therefore be made by managers to either minimize their purchases of new land for water or waste treatment purposes or to increase the capacity of facilities already in operation.

In many instances, this means greater use of chemicals since the equipment already installed cannot be easily changed or replaced. In new installations, more efficient equipment of either a mechanical or biological nature will help the situation, but even in these cases, specialty and bulk chemicals should play an important role.

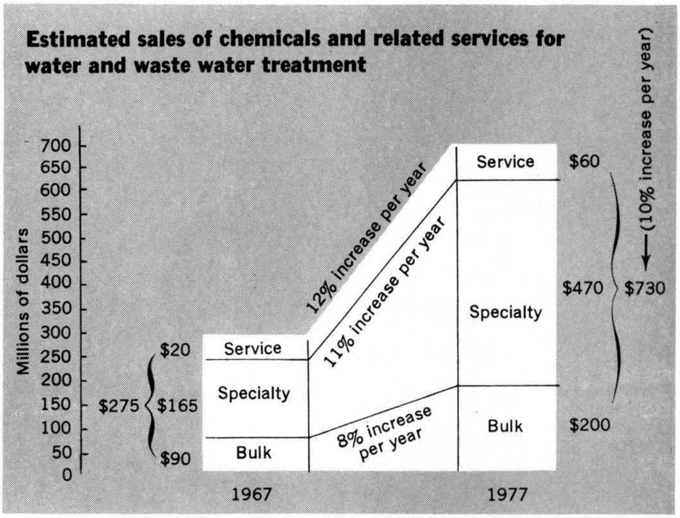
**Greater emphasis on operating costs.** Ordinarily, the construction of waste treatment facilities adds nothing to the operating or manufacturing capability of an industrial plant—other than allowing it to continue operations at the same stand! Since the demand for capital usually outweighs the availability, corporate management wishes to make the most effective use of the funds at its disposal. Given this set of conditions, there is considerable pressure to reduce as far as practical the capital outlays necessary for waste treatment facilities. On the other hand, plant operating costs, including expenditures for chemicals, are a deductible item on the profit and loss statement.

**Joint treatment plants.** Where waste streams are compatible, it is often to the advantage of both industry and municipalities to combine their waste streams and treat in a central location. In certain cases, however, special pretreatment of wastes may be required to render them acceptable to the joint treatment plant. Here, all segments of water and waste treatment—chemicals, equipment, and instrumentation—can be expected to play important parts.

**Water augmentation.** Over the long term, the demand for water in some areas will gradually exceed the available supply. Industries and towns will therefore turn to means of augmenting their water supplies through water importation, more extensive methods of recycle and advanced waste treatment, or the demineralization of low quality water supplies. With the possible exception of water importation, these alternatives imply increasing usage of chemicals.

For these reasons, I believe the future for chemicals in this field is indeed an attractive one. Sales of chemicals and related services can be expected to grow from approximately $270 million this year to at least $730 million over the next 10 years. On the average, this projection reflects something in excess of a 10% increase per year, with the most rapid growth occurring in the service area, about 12%: followed by specialty chemicals, 11% per year; and bulk chemicals, about 8% per year.

Finally, we should give some thought to the manner in which the water and waste treatment industry (and more specifically, the chemical segment within that industry) has operated, and how it may function in the future.



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The industry as a whole—including equipment, chemicals, instrumentation, construction, and all other areas—has been typified by relatively modest growth and change over the past several decades. Within that time span, the specialty chemical segment has shown the greatest growth, profitability, and technological advance, spurred by the varied needs of its customers, primarily in the chemical process industry.

Historically, the water and waste treatment industry has been quite segmented, with each area defined as a function of its rather specialized products, different customers, and significant differences in marketing philosophy and approaches. In addition, the industry has been characterized by the participation of only a relatively few companies that could be considered actual or potential major factors, particularly in the more specialized portion.

### Expanding field

There are, however, indications of change. A number of companies heretofore not involved directly in water or waste water treatment have become participants, either through acquisition or through internal developments of their own. An illustration of the former is the recent acquisition by Hercules of Aquatrol, a specialty chemical firm in Houston. The development of the Permasep process by Du Pont was mentioned earlier. These new participants in the field are large companies, often heavily service-oriented.

Another development has been the increased emphasis placed upon technical service, which is now being increasingly offered in connection with both influent and effluent treatment and, to an increasing extent, by equipment and instrumentation suppliers. This type of service extends all the way from problem definition to development of a solution to that problem through maintenance and repair.

Another development, more difficult to define but nevertheless occurring and certainly on the mind of many would-be entrants to the field, is the gradual trend toward integration of the various specialized segments of the industry which heretofore have been separated.

In the future, the chemical companies which participate in the water and waste treatment industry probably will display a more functional integration of several disciplines, with a single company offering a more complete line of specialized products and services from surveys through the supply of its own equipment and chemicals to perhaps even maintenance and operation of the facilities themselves.

In any event, over the next 10 years, this segment of the chemical industry will probably exhibit rapid growth and increasing sophistication, and bear great responsibility for the quality of the environment in which we live and work.

As industrialization and urbanization become more intense, municipal water supply managers are facing considerably more problems than ever before on

# Tastes and Odors in Water Supplies

**James C. Vaughn, Department of Water and Sewers, Bureau of Water, Chicago, Ill.**

Problems of taste and odor in water supplies began to appear in numerous areas of the United States during the 1920–30 period. Industrial production was at a high rate for the times and there were unlimited discharges of both industrial and domestic wastes to the surface water supplies of the country in urban areas. With the development of a luxury-conscious group within the population, the criticism of objectionable tastes and odors in community water supplies became quite general. In many urban areas, the water consumers completely abandoned their municipal water supply for drinking water and resorted to bottled water from various sources.

In 1932, John R. Baylis, chief physical chemist in charge of Chicago's Experimental Filtration Plant, made a survey of 58 water plants throughout the country. Of these 58 plants, 26 reported objectionable tastes and odors as originating from various forms of algae. Thirty-two of these plants reported objectionable tastes and odors as originating from industrial wastes. This should give some idea of the general prevalence of concern by the operators of municipal water plants with the problem of tastes and odors. The operators of the municipal systems desired, even then, to improve their public image, and conducted much research in the areas of preventing or eliminating these objectionable tastes and odors.

Baylis began his work in this area at the Chicago plant in 1928, following a period of very disagreeable chlorophenol taste in the drinking water of Chicago during December 1927. This is described in his most important book, *Elimination of Taste and Odor in Water,* which unfortunately is out of print. Three copies of this book will be available for those who are interested in looking at it on the premises in the John R. Baylis Memorial Library at the Central Water Filtration Plant, 1000 E. Ohio Street, Chicago, Ill., when the library opens in the near future. In this book, Mr. Baylis described his experiments with granular and activated carbon, superchlorination, potassium permanganate, and ozone. He also discussed at length the various concepts of the ammonia-chlorine method of preventing chlorophenol odors.

### Types of treatment

In the 1932 survey, Baylis requested a report on the various types of treatment used at the reporting plants in attempting to prevent or eliminate the objectionable odors encountered. They reported as follows: aeration, 2; activated carbon, 19; ammonia-chlorine, 28; chlorination, 5; superchlorination followed by dechlorination, 3; potassium permanganate, 3; potassium permanganate and chlorine, 2; ammonia-chlorine and carbon, 2; potassium permanganate and carbon, 2; and excess lime, 2. A number of the plants tried several forms of treatment, which accounts for the fact that the number of plants using the various types of treatment totals more than the 58 plants surveyed.

The fact that Baylis' survey made in 1932 showed that 19 water plants were using activated carbon shows how much progress had been made in developing a market for this material

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**Queue.** *The demand for purified drinking water was so great in Chicago in the early 1930's that people waited in long lines to fill jugs with water from the recently installed activated carbon units*

since the beginning of his work at the experimental plant in 1927. Research proving the beneficent effects of a given product are meaningless unless the product is brought to the attention of the potential users. Baylis did the experimental work which proved the general application of powdered activated carbon.

### Chlorophenol tastes

Baylis began his experiments on the elimination of tastes and odors following an epidemic of severe chlorophenol tastes in Chicago's water supply. At that time, there was no accurate and dependable method for determining the amount of phenol in a water supply either before or after treatment. Accordingly, he, with the aid of Oscar Gullans, began work on the development of such a method.

A method developed by Gibbs was modified by Baylis and Gullans so that it detected phenols at the levels existing in the raw water supply. This method (using 2,6-dibromoquinonechlorimide as the indicator) will detect concentrations as low as 5 parts per billion of phenol in water—without preconcentrating the sample. The method is time-consuming, but in the hands of a good chemist, can be very accurate. The colors have to develop over a two-hour period. Better results were obtained by permitting the color tubes to stand overnight. Working in conjunction with Gullans, results within a range of 0.5 units of a phenol value in the 15–17 range were obtained. This method is still used at Dallas.

Another procedure that came into being during this period was one requiring a much shorter time in which the color-forming agent was diazotized sulfanilic acid. This procedure was subject to erratic results and much deviation on check samples between different laboratories, and was finally abandoned by the AWWA Activated Carbon Standard Committee. It is still in use in Europe, however.

In the post-World War II period, the method using 4-aminoantipyrene as an indicating agent came into general use. This method is much less time-consuming and gives more precise results, although some difficulties have developed in recent months with this material. Much work is going on endeavoring to resolve these difficulties.

### Odor intensity

In addition to a method for determining phenols in water, a method for quantitatively evaluating the odor intensity of water was needed. Many people contributed to the development of the method that is now in general use. The original idea, that water containing odor be diluted with odor-free water to the point where the odor is just detectable and that this dilution be called the threshold odor number, was originated by C. H. Spauling.

Over the years, the threshold odor test has been much refined, and modified attempts have been made to automate the tests. In the food and flavor industry, some success has been obtained in this way, but pure compounds and comparatively high concentrations of specific odors are involved here. In the water treatment industry, the threshold odor test is probably the most acceptable method of evaluating the taste and odor quality of untreated and finished waters.

Dr. Aaron A. Rosen, Head, Organic Contaminants Study, Cincinnati Water Research Laboratory, FWPCA, told the Technical Advisory Committee of the Federal Water Polution Cal-

**Comparison.** *As the citizen collected his purified water from the activated carbon units he was reminded quite vividly of the appearance of the water before treatment*

umet Area–Lake Michigan Conference on July 22, 1965, that the threshold odor test if properly done with odor panels (two or more persons experienced in odor detection) is a fairly reliable test giving, under these conditions, 20–25% variation in results.

Considerable effort was made by the several manufacturers of powdered activated carbon during the late 1930's to establish the threshold odor test as the sole method of evaluating the adsorptive capacity of activated carbon. Their point of view was that the satisfactory performance of a given carbon in adsorbing a taste and odor should be the only standard of performance. With the 20–25% variation in threshold odor results, this standard would have given the manufacturers a rather wide quality range by which to measure their product.

### Carbon evaluation

From July 1936 to March 1943, when I was a chemist and superintendent at the Hammond, Ind., water filtration plant, this plant lent itself very well to comparative carbon evaluation tests. The quality of the raw water before any treatment may be measured and one brand of activated carbon could be applied to one mixing and settling basin, and another brand could be applied to another mixing and settling basin. By determining the quality of water from each basin, the relative taste and odor removal capacity of each carbon could then be determined.

In 1937, such a series of tests was conducted at this plant. The carbon under contract was used as a basis of comparison, or reference carbon, and was run against each of four other brands of carbon. Each company supplied, without charge, two carloads of their carbon and a chemist to assist in running the test.

The tests were run and the results evaluated and reported in a paper, "Experience with Activated Carbon at Hammond, Ind." The results of the test showed conclusively that the relationship between the parts per million of activated carbon required to remove one threshold odor unit and the phenol value was in direct proportion to the phenol values of the different carbons. This paper did much to establish the phenol value as a reasonably accurate and reproducible method of measuring the adsorptive capacity of powdered activated carbon.

### Phenol value

Perhaps at this point, it would be desirable to give a definition of the term *phenol value.* The phenol value of activated carbon is the number of parts per million (p.p.m.) of carbon necessary to apply to a solution of 0.1 p.p.m. of phenol in distilled water in order to reduce that concentration of phenol to 0.01 p.p.m. Consequently, the lower the phenol value of a given carbon, the greater is its adsorptive capacity. For example, only three fourths as much carbon with a phenol value of 15 would be required to remove 0.09 p.p.m. phenol as it would for a carbon with a value of 20.

Since having established at Hammond that the threshold odor adsorptive capacity of activated carbon was proportional to the phenol value (the lower the phenol value, the greater would be its threshold odor removal capacity), it was easy to prepare curves for the carbons of different phenol values showing the parts per million of carbon that must be applied to reduce the threshold odor of a given raw water to the finished threshold odor value of 3, which was the maximum desirable at that time.

Since all water plant chemical feeders are calibrated in pounds per hour and the rate is set according to the pumpage in million gallons per day, it was necessary to prepare curves from which the plant operators could set the desired application rate of activated carbon for a given threshold odor of raw water at the current rate of pumpage. This practice is still in vogue in most water plants that apply powdered activated carbon.

### Industrial pollution

In tests at the Whiting Filter Plant, which suffered from an extreme degree of industrial pollution, the effectiveness of chlorination, ammonia-chlorine treatment, chlorine dioxide, ozone, clay, chlorinated copperas, and activated carbon were studied. Work done in the laboratory on free residual chlorination showed that the chlorine demand of the raw water ranged from 20–50 p.p.m. and left the water with a burnt acrid taste. It also reduced the threshold odor only to a certain point, beyond which it became ineffective. Chlorine dioxide was also tried, producing the same result as free residual chlorination—reducing the threshold odor to a given point and no further, and leaving the water with a burnt acrid taste. For instance, the threshold odor number of a particular water sample was lowered from 28 to 12 , but no further reduction could be obtained with chlorine dioxide.

Where waters contain large amounts of phenol, the treatment of the various corrective agents for removing this phenol may become prohibitively expensive, if not physically impossible. Harold and Adams established in England that the use of ammonia before chlorination would produce an aminophenol, and that subsequent chlorination would then produce a tasteless and odorless chloroaminophenol. McAmis at Cleveland, Tenn., was the first water plant operator in the United States to apply ammonia before chlorination to prevent chlorophenol tastes. This was, and is practiced quite successfully at the Hammond, Ind., water plant. This treatment was tried at the Whiting plant during these experiments and while it was necessary to reduce the ammonia-chlorine ratio from 4:1 to 3:1, the treatment was successful in preventing chlorophenol tastes, and is still being practiced there.

Some experiments were conducted on the use of granular activated carbon filter. The results were quite disappointing. The carbon soon lost its ability to act as an effective taste and odor reducing medium. This phenomenon can be attributed only to the fact that very heavy loads were placed on the filter at all times. The threshold odor of the water passing through the filter ranged from 20 to 100.

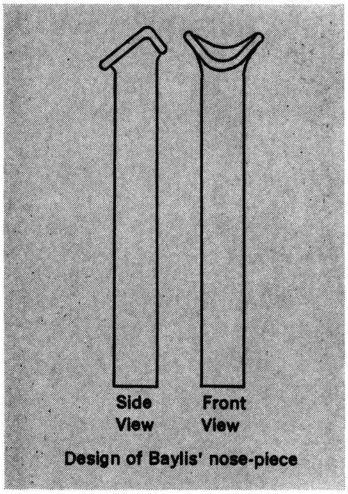
Whiting had been operating an ozone plant for nearly eight years. Soon the technicians discovered that one could not produce a completely odor-free water, even by distillation, from water that had been treated with ozone. Therefore, the ozone treatment was discontinued for a while. Treatment was then begun on a plant scale with powdered activated carbon alone. The threshold odor value could then be reduced to any desired point, if enough carbon were added. The maximum dosage required to do this reached as high as 140 p.p.m. of carbon.

One of the problems at this time, at the Whiting water plant, was the appearance of a considerable amount of film oil on the surface of the raw water. By the application of dry fuller's earth to the surface of the raw water and later coagulation with chlorinated copperas, the surface oil was effectively removed.

### Ozone

The practice at the Whiting water plant was to apply ozone to the incoming raw water ahead of two diffusion towers. The capacity of the ozonators limited a maximum application to 4.8 to 5.4 p.p.m. It was the general practice to ozonate, when possible, to a slight residual of approximately 0.1 p.p.m. using *ortho*-tolidine as the indicator, with the usual chlorine standards.

This work at Whiting is described in detail in a paper, "Experimental Studies of Odor Control at Whiting, Indiana." For reasons best known to the operators of the Whiting water plant, ozonation is still used there.



Design of Baylis' nose-piece

In the Whiting studies, little success was obtained in the use of granular carbon filters, largely because of the heavy loads placed on them. During the period when most of the development work was going on in the activated carbon field, there were a number of cities that employed granular carbon beds on top of their regular filters. The granular carbon used in these filters was light and in order to retain the carbon on the filters during the backwashing period, retaining screens had to be installed above the carbon layer. This interfered with the normal backwashing of the filter and the carbon soon lost its effectiveness when the loads were heavy. The practice of using granular carbon filter beds soon died out.

The carbons available during this period were low in specific gravity and large in particle size (4 to 8 mesh). The use of this carbon in pressure filters was, and has continued to be, satisfactory. The rate of flow through these filters must be very low or the action of the bed becomes simply a "polishing" reaction.

In recent years, a form of granular carbon with a mesh size ranging from 8 to 30 for one grade, and 12 to 40 for another grade, has appeared on the market. This material has a particle density (g./cc.) of 1.4 to 1.5. It is being recommended for use in filter beds of depth ranging from 2.5 to 7.5 feet. These beds do not require retaining screens to hold the material in place during backwashing.

Carbon used in this manner performs the dual functions of turbidity removal and taste and odor removal. The material also can be reactivated.

**Monitoring.** *Probably the most widely acceptable method of monitoring the taste and odor quality of untreated and finished waters is with the help of the Baylis nose-piece*

### Potassium permanganate

In the survey made by Baylis in 1932, seven water plants reported using potassium permanganate as a taste and odor removal aid either alone or in conjunction with other threshold odor removal agents.

In recent years, the use of potassium permanganate has attracted much attention. This is due to a paper by A. K. Cherry published in 1962, "Use of Potassium Permanganate in Water Treatment." This application was at Cedar Rapids, Iowa. The assumed probable cause of the difficult tastes and odors was indicated as algae and actinomycetes. Costs of the treatment with permanganate and with activated carbon are given. Carbon as the second agent used together apparently produced a satisfactory finished water.

### Chicago's water supply

The sources of objectionable tastes and odors in Chicago's water supply include those sources that might be called natural, coming primarily from various forms of plankton. When the total plankton count is high—in the 30,000 to 40,000 units/ml. range—the water may acquire a musty, fishy smell. Occasionally, the water has the characteristic pigsty odor which is due to the presence of *anabena*. On other rare occasions, the raw water has a musty, moldy taste and odor which is traceable to a mold organism similar to, but not truly, actinomycetes. The most objectionable plankton odor is that due to dinobryon. When the number of these organisms amounts to 30 or more per ml., the water has a taste and odor similar to that of cod liver oil.

The most extreme tastes and odors, of course, come from industrial wastes. These range from volatile hydrocarbon, kerosine-like, and pungent musty chemical to burned garbage. While phenol-like substances are frequently found in hydrocarbon pollution, it is seldom in concentrations high enough to give the water a characteristic phenolic odor until it is chlorinated. Then the chlorophenol odor is very apparent even in very minute concentrations. The chlorophenolic odor nearly always occurs in the presence of other hydrocarbon wastes. This does not make it any less objectionable.

Occasionally, the water has a musty, septic odor which is more or less characteristic of sewage plant effluents.

### Treatment practices

The practices of water treatment that are followed at Chicago's two filtration plants bear some description. Plankton odors can usually be removed by excess chlorination, except in high concentration. In this case, activated carbon may be added to the water before all other treatments. Treatment facilities at the South Plant are so designed that either carbon or chlorine may be added to the water 1100 feet ahead of other chemical treatment.

These two agents are never added simultaneously. In the case of high concentrations of hydrocarbon wastes, or dinobryon (fishy) odor, the carbon is added at the distant point and chlorine at the entrance of the mixing basin. This is very necessary when phenol-like substances are present in any measurable concentration for, when phenols are chlorinated, the rate of adsorption of the chlorophenol onto activated carbon is very low. In the case of high concentration of hydrocarbon wastes, it is desirable to add most of the activated carbon at the distant point ahead of all treatment and apply the remainder at the beginning of the mixing basins. This split treatment gives much more effective use of the carbon.

At the Central Plant all chemicals are normally applied in application channels several hundred feet before the entrance to the mixing basins. Chlorine can be applied, at present, in the intake basin just ahead of the low lift pumps. When all tunnel connections have finally been completed, either carbon or chlorine can be applied in the tunnel approximately 1200 feet ahead of the intake basin.

### Carbon slurries

There have been two developments in Chicago that have facilitated application of the large amounts of carbon that are frequently required for the elimination of high concentrations of objectionable tastes and odors. One is the development of application of carbon in slurry form. The carbon is received in bulk form in hopper cars containing 2600 cu. ft. of carbon.

The carbon in the car is first fluidized for 30 minutes with low pressure air, then discharged into square concrete tanks containing some water and equipped with turbine mixers operated at roughly 55 r.p.m. After the car is unloaded, the slurry is diluted until it has a concentration of 1 pound of activated carbon per gallon of slurry. It is then pumped to storage tanks and then to feeding tanks from which it is applied through suitable metering devices to the point of application. At the South Plant these devices are rotating wheels discharging 1 gallon of slurry for each rotation of the wheel. At the Central Plant, the slurry application is metered by magnetic flowmeters.

### Continuous odor monitor

The second device developed at Chicago for elimination of tastes and odors is the continuous odor monitor. The Chicago water system is unique in that it has no reserve storage. Consumption must be met with production for every hour of every day. The water cannot be treated on a batch basis until its quality is acceptable in all respects.

The continuous odor monitor was originally conceived by H. H. Gerstein, former chief water engineer, now retired. The staffs of both filtration plants have worked to modify and improve the device. The principle of the device is continuously pumping small amounts of water through a heating mechanism and spraying it through a nozzle into an open top bell jar. The heating mechanism is adjusted so that water enters the bell jar at the proper temperature for the threshold odor test (about 140° F.).

At the South Plant, Chromalox electric heaters are used for this purpose. At the Central Plant, all of the lines going to the several odor monitors pass through a hot water tank which is thermostatically adjusted so that the water is discharged to the odor monitors at the proper temperature.

During the periods of sudden and critical change in the threshold odor values of the raw water, the supervising engineer, the control engineer, and the control chemist make frequent observations, with the aid of a Baylis nose-piece, of the odors of the raw and treated waters in these monitors. This gives them an instantaneous qualitative estimate of the threshold odor intensity of the raw water. Adequate changes in carbon application may be quickly made and later adjusted on the basis of the threshold odor dilution test, which takes about 20 minutes to run.

The general principle that is applied on such occasions is, "go up with carbon dosage with dispatch, come down with discretion."

### FWPCA conference

In March 1965, the Federal Water Pollution Control Administration for the Calumet Area and the Southern End of Lake Michigan, held a conference in Chicago in which the nature and degree of pollution were reported upon by a number of groups concerned.

Following this meeting a Technical Advisory Committee was assigned the task of drawing up the criteria by which the water quality of Lake Michigan and its tributaries would be evaluated. This committee held a total of 24 meetings under the chairmanship of F. W. Kettrell and agreed on 24 parameters. These were adopted as official by the conferees in a meeting in January 1966.

The passage of the FWPCA Act in 1965 and the activities of the conference should have resulted in a definite and immediate improvement in raw water quality. However, this has not been the case. On the contrary, there has been a steady deterioration of raw water quality, especially with regard to the open waters of Lake Michigan.

The average daily carbon dose at the South Plant rose from 23 lb./m.g. in 1965 to 43 lb./m.g. for the first half of 1967. The maximum dosage in lb./m.g. was 230 in 1965 and 400 for the first half of 1967. The average ammonia nitrogen was 0.017 p.p.m. in 1965, 0.028 in 1966, and 0.038 for the first half of 1967. This means that this value has more than doubled in 2½ years. The maximum ammonia nitrogen values were 0.111 p.p.m. in 1965, 0.126 p.p.m. in 1966, and 0.376 p.p.m. in the first half of 1967. This represents a steady and rapid degradation in the quality of the raw water at the intake of the South Plant.

At the Central Plant, the average carbon dose did not show much variation, but the maximum carbon dose did show a very sharp increase. This is also true of the average and maximum ammonia nitrogen values.

### Tastes and odors

Of the 24 parameters adopted as official in January 1966 by the conferees of the FWPCA for the Calumet Area and the southern end of Lake Michigan for open waters, four parameters are considered important as related to tastes and odors. They are threshold odor, ammonia nitrogen, phenol-like substances, and total phosphates, the latter being significant because of their contribution to the growth of plankton and the ultimate effect of plankton on tastes and odors. The daily average value of these parameters has increased and shows a progressive deterioration of raw water quality in the southern end of the lake.

The increase in the use of the three critical chemicals—coagulants, carbon, and chlorine—has resulted in a steady and sharp increase in the chemical costs in treating raw water in Chicago. Price increases account for part of the total cost increase but by far the major reason for the increase is the degradation in the raw water quality.

### Cost per unit

Nowhere, except in the description of the early work at Hammond, has it been stated that one can determine the cost of removing one threshold odor unit of a given odor characteristic. In the two Chicago filtration plants, each supervising engineer is held responsible for producing a treated water that is always palatable, with a maximum threshold odor of 1.5. This results in quite a variation of interpretations of the required dosage. Volatile hydrocarbons and kerosine-like odors require the lowest dosages of activated carbon while the musty chemical odors and specific chemical wastes require the higher dosages. In general, the requirements range from 1 p.p.m. to 4 p.p.m. of activated carbon for each threshold odor unit removed.

It is a matter of great pride to the Water Purification Division that the number of customer complaints in Chicago on tastes and odors in the finished water from both filtration plants has been at a minimum.

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# QUOTE...

## TECHNOLOGICAL CHANGE, A NATIONAL NECESSITY

The alteration of the physical as well as the social environment is not a recent phenomenon. Our so-called ecologic crisis has historical roots. We are all aware that the virgin forests of North America which greeted settlers two centuries ago have now largely given way to cultivation or to urbanized settlement. But, as Lynn White of the University of California has recently pointed out, we can look further back into history at decisive alterations in man's environment. [But] what is it in the process of environmental change which is fundamentally different? Why are we concerned now rather than 100 or 1000 years ago?

I suggest that the problems today are not necessarily different in kind but are so much more widespread and grow in severity so much more rapidly that we can no longer afford to respond passively only after they become obvious. In the past, people slowly became adjusted to a polluted river here and a smokey valley there. These became facts of life for man to live with as best he could, or to move to a more salubrious environment. Now, the pace of change results in dramatic environmental changes over a decade rather than a century. We all know from personal experience that the air pollution in many large cities has gotten significantly worse in the last few years. Many of us are familiar with streams once clear in our youth which are now virtually unrecoverable. Within a man's lifetime the automobile has changed social patterns, land usage, the fundamental nature of the community and the family.

What is new is the scale, variety, and speed of change, both in man's physical and his social environment.

When studying pollution problems, traffic congestion, and needs for recreation areas it is tempting to recommend a moratorium on change—at least until we catch our breath on the 20th Century treadmill. But we all realize that this is out of the question—we would not want to pay a fraction of the price of technological stagnation. Technological change is a national necessity in a modern world. Continuing, pervasive advance in the way we do things and in the products and services we consume is the engine which permits us to satisfy the most critical needs of an expanding population characterized by continually rising aspirations. It is not true, as is sometimes said, that we have mastered the problems of production. Unless we manage to sustain or increase our present rates of increase in per capita gross national product, and to improve the distribution of the product, we will be unable as a nation to find the resources necessary to: • Maintain security. • Overcome poverty at home. • Reduce the gap between rich and poor countries. • Improve our environment. • Find solutions to pressing problems of natural resource and food supply.

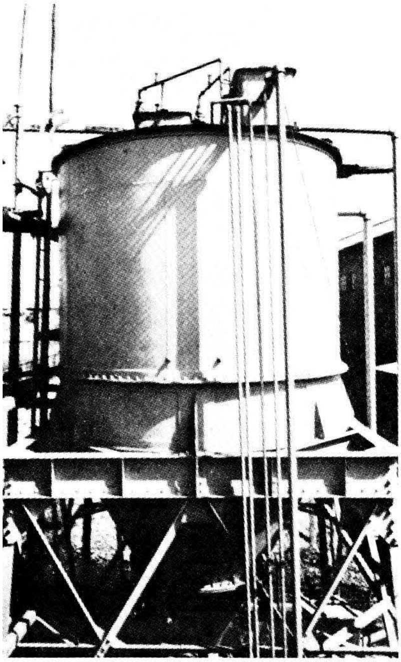
**Dr. Donald F. Hornig**

Director, Office of Science and Technology,
Executive Office of the President,
before the Subcommittee on
Intergovernmental Relations, Senate
Committee on Government Operations

**Shuzo Nishihara,**
**Nishihara Environmental**
**Sanitation Research Corp.,**
**Ltd., Tokyo, Japan**

# A River Can Be Made to Help Itself

River's natural capacity for self-purification helps minimize the costs of pollution control and provides unexpected opportunity for unusual recreational benefits



Experimental plant

The most important task in cleaning up the Sumida River is to find a satisfactory way to treat a large quantity of waste. Basically, we consider it necessary to reduce substantially the concentration of pollutants in the sediments in the river, sea, and seashore, where they have been accumulating for several decades, and require factories to install reasonable primary treatment plants according to the permissible limit of their wastes. When these measures are put into practice and the settleable solids are removed from wastes, water could be kept clean by the river's natural capacity for self-purification. Keeping these goals in mind, we designed a system of portable treatment tanks under central control.

### Preliminary pilot plant

The Tagara River is a small stream that flows through Itabashi Ward, Tokyo, where there is no central sewage system. The stream is considerably polluted by a large quantity of domestic sewage and a relatively small quantity of industrial wastes.

The experiment at the Tagara River was a pilot plant operation preliminary to the clarification of the Sumida River. Since the Sumida River has a large volume of flow, we decided to utilize the river's natural capacity for self-purification so as to minimize operational costs, particularly the cost of electric power, and simplify construction and operation. Thus, we set the treatment rate at 40 to 65%, and assembled all the unit processes in one tank.

### Treatment tanks

The tank is circular, with pumps and pipe gallery in the core, mixing chamber and sludge aeration chamber in the middle, and a sedimentation chamber on its circumference.

In each tank, three different types of vertical axis pumps are installed in the center gallery, and two regular air compressors and one spare are installed in the pump room, which is located between two such tanks.

An automatic control apparatus for each tank is also installed in the pump room, and two tanks are controlled as a unit. Each automatic control apparatus is operated from the group control center.

The intake is a wooden frame filled with gravel. At the center of the frame, perforated reinforced concrete piping is installed. Because of the intake, such facilities as grit chamber, screen, and primary settling tank can be eliminated.

In the sludge aeration chamber, 168 mechanical air diffusers are installed, and in the mixing chamber 168 jet diffusers (stream water and compressed air diffuser) are installed.

Sludge aeration chamber detention time is 120 minutes; mixing chamber detention time, 23 minutes; and sedimentation chamber detention time, 100 minutes.

### Installation

These treatment tanks would require a large surface area if they were constructed on land. For this reason, we decided to install the treatment plants on and over the surface of the river, and to utilize the top slabs of the tanks, made of precast concrete plates, for various facilities such as parks, heliports, playgrounds, parking areas, restaurants, athletic grounds, and the like (see ES&T, February, page 173, for a Japanese hotel and amusement complex built atop a sewage plant).

Three methods for installing the treatment plants on the river were contemplated:

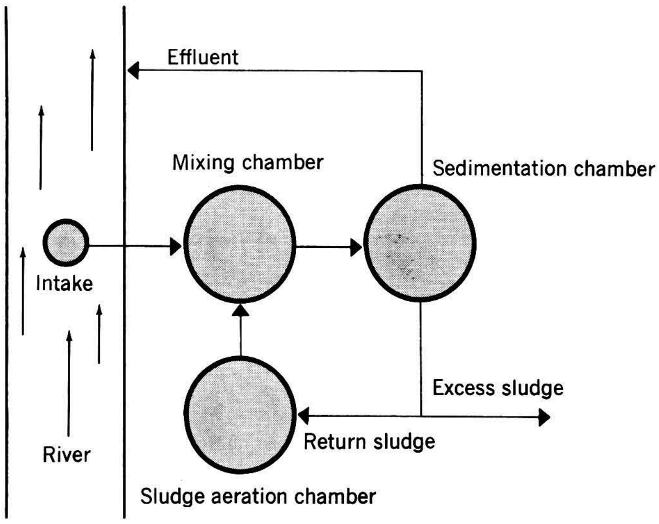
- Installing the plants on the surface of the water.
- Fixing in the water.
- Floating.

There are certain advantages and shortcomings in each method. Therefore, taking into consideration such factors as variation of water level of the river, depths of the river, shape and function of the treatment plant, the combination of the three methods has been adopted. Part of the weight is supported by piers, part by submerging a portion of the tank in the river, and part by floats. This method is considered to be the most reasonable way to satisfy all the conditions.

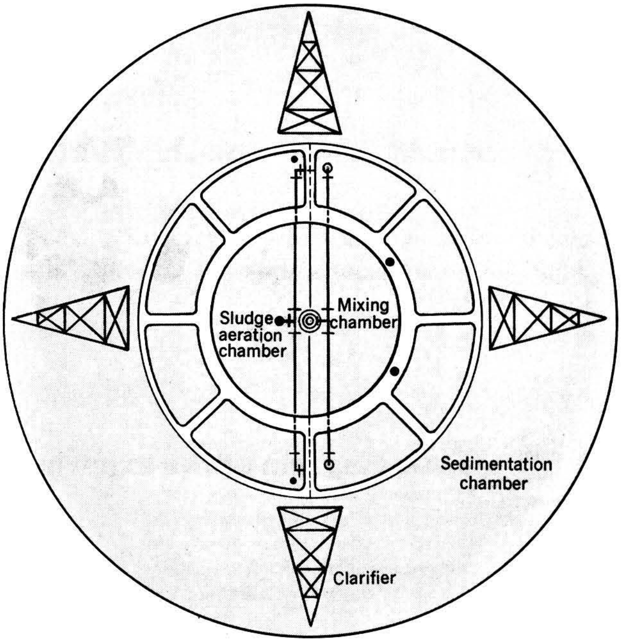
### Subunits

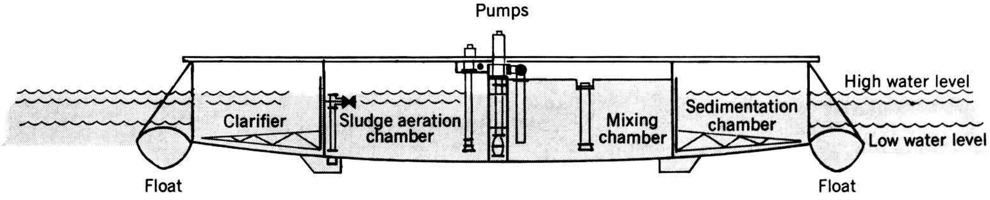
The main structure of the tank consists of a compression arch frame and bottom membrane. Each tank—a plant unit—is manufactured in 16 subunits. A subunit consists of an arch frame, a bottom membrane, an exterior shell, an interior shell, a float, and a net-cylinder for mounting the float.

## Flow diagram of the experimental plant



## Cross sections of the high-rate activated sedimentation tank





Each subunit manufactured at the factory is sent to the dock, where all are assembled in one large unit and equipped with a protection net. When the assembling is completed, the unit is floated and towed to the setting point in the river and fixed on the 16 pre-installed piers.

When preliminary treatment plants for wastes are installed in factories, and when the river becomes clarified, the tanks can be released from the piers and floated and towed to other polluted rivers.

### Sumida River

The Sumida River is a branch river of the Arakawa River, and its flow is controlled by the sluice gates at Iwabuchi. There are two more sluice gates, one at Horikiri (11 kilometers downstream from Iwabuchi) and one at Azuma (which is 3.5 kilometers farther down the river). The flow of two flood control canals, the Arakawa Canal and the Nakagawa Canal, as well as the flow of the Sumida River, is controlled by interchanging water by these three sluice gates. The gates protect Tokyo metropolitan district from flooding.

Tokyo metropolitan government has a 5-year plan to dredge the Sumida River. From the mouth of the river to the Joban Railroad (9 kilometers upstream) is scheduled to be dredged to a depth of at least 3.0 meters, and from there to the Iwabuchi sluice gate is to be dredged to a depth of at least 1.8 meters, with a grade of 0.0001 for the distance of 12 kilometers from the starting point.

The flow of the Sumida River is 85.0 cu.m./second, with 71.5 cu.m./ second back flow of sea water at high tide.

The Shinkashi River flows in at the upper boundary of the river.

### Pollution sources

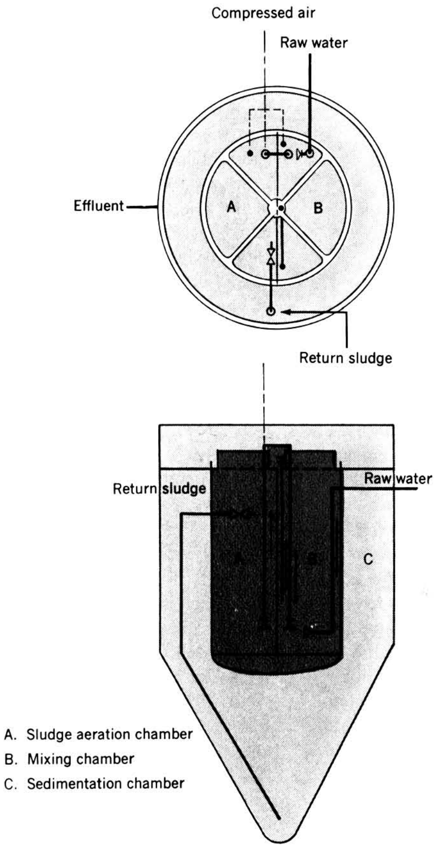
Of approximately 2000 factories along the Shinkashi River, 320 factories should be required to install complete pretreatment plants. Wastes from the Shinkashi River are responsible for 27.6% of the total pollution of the Sumida River. There are 6000 factories along the main stream of the Sumida River, of which 260 should be required to install pretreatment plants.

**Pilot plant specifications**

| | |
|---|---|
| Influent | 83.4 liter/minute |
| Sludge return rate | 20% |

| | Detention (minute) | Volume ($m^3$) | Air volume (liter/minute) |
|---|---|---|---|
| **Mixing chamber** | 20 | 2 | 76 |
| **Sludge aeration chamber** | 120 | 2 | 76 |
| **Sedimentation chamber** | 90 | 9 | — |

## Experimental plant for high-rate activated sedimentation process



Two other branch streams contaminate the Sumida River, too. One, from Koto District, is responsible for 37.7% of the pollution of the Sumida River (its wastes are 92.0% industrial); the other is the Kanda River, which contributes 26.4% of the pollution load (its wastes are 13.0% industrial and 87.0% domestic sewage).

In the Koto and Senju Districts, the main source of pollution is small-scale plating factories—almost 10,000 in number. There are also small meat factories and dye factories which discharge highly polluted wastes. As these small factories have no legal obligation to install pretreatment plants, the government must provide necessary pretreatment plants at public expense.

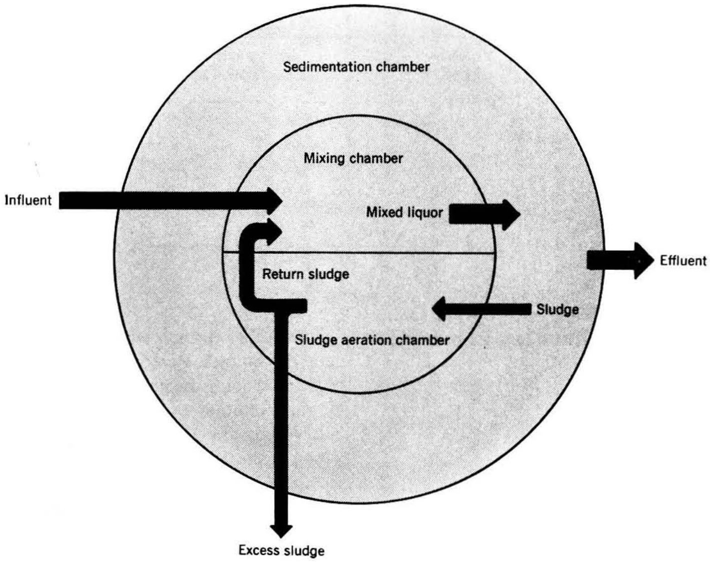
Dumping of refuse and night-soil into rivers is another source of pollution. Strict control of these activities is also necessary. Otherwise, the Sumida River will never be cleaned up.

### Survey of factories

A survey of factories, including analysis of wastes and processes of production, was conducted preliminary to designing suitable pretreatment plants for each factory. Twenty-five factories were intensively investigated by Dr. F. Nakajima. Wastes were classified as food industry, paper industry, chemical industry, metal industry, cement industry, or dye industry. Wastes from 24 of these factories—all but one—are discharged into the Shinkashi River.

Separate tabulations were prepared for wastes which are discharged continuously and those which are discharged intermittently. Continuous wastes are separated into cooling water, which does not need to be treated (and in fact can be used as dilution water), and wastes which require treat-

**Flow diagram of the high-rate activated sedimentation tank**



ment, and the percentage to total volume of discharged water was calculated for each. Indexes of pollution, such as COD and acidity and their percentage to preceding factors, were also classified by industry. Volume of water required for a ton of product and typical analyses of mixed wastes were recorded, too.

Armed with this information, we undertook the pilot plant operation outlined at the beginning of this article.

### Personal experiences

During my studies of the ever-increasing industrial waste problem, I have come across a number of instances of pollution, and I would like to recount some of my personal experiences.

On December 15, 1961, at the seashore of Kanazawa Hakkei, Kanagawa Prefecture, laver (seaweed) was damaged by the plating waste discharged from a nearby factory. The waste destroyed the cellular tissue and brought about decolorization of the laver by disintegrating pigments, which resulted in 30 to 40 million yen worth of annual injury. At the same time, fry of the goby fish were killed and floated up on the surface of the water.

An investigation revealed that the damage was caused by the waste overflowed from a plating bath of an automobile factory. The waste was being discharged without sufficient treatment.

Since this had been a favorite fishing resort of mine for almost 40 years, I presented the data on laver damage to the automobile factory through the director of the local fishermen's union on February 4, 1962. But while the negotiations dragged on, the swimming season drew near. Since the place was a summer resort as well, on June 30, 1962, I again presented a request, this time in my own name, to the factory, through the director of the union, to provide separate piping for plating wastes, store the wastes in a holding tank, and give suitable treatment before discharging it to the sea. I requested the factory to treat strong acid wastes using the same method, too.

This suggestion was implemented, and there was no harm during the swimming season. Laver recovered by December 30, 1962. However, there was some reduction in yield due to the unusually low water temperatures which occurred in January 1963. At present, there seems to be no damage by sodium cyanide.

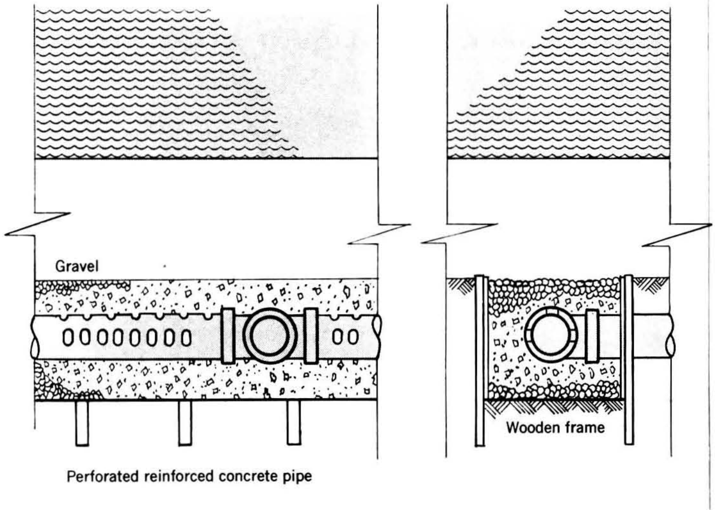
The case mentioned here is evidence that relatively simple pretreatment can prevent damage when plating bath wastes are to be discharged into the sea. A small quantity of the sodium cyanide contained in the wastes can be diluted by sea water, or aerated by the turbulance of the waves, and it will become harmless.

The place, Kanazawa Hakkei, is a well known and historical place, known particularly for the Kanazawa Kunko (an old library which dates from before 1312) and its beautiful scenery, laver cultivation, and the beautifully maintained beaches—one of the best swimming resorts in Tokyo Bay during summer time. It is very fortunate for public welfare that this lovely place is no longer injured by dangerous industrial wastes.

On February 22, 1962, after the incident of the first automobile factory, another incident occurred—caused by the waste discharged from another automobile factory in the suburbs of Fujisawa City. Waste was discharged to the small stream, where there is an intake of dilution water for Fujisawa City Night-Soil Treatment Plant nearby downstream. The digestion tank of the night-soil treatment plant was badly affected by the waste, and its gas production dropped to one third of its ordinary level. At the same time, 250 roach (a species of fish), which were grown in a pond of the treatment plant, were killed, because the pond used the water from the same river. In this case, we presented a letter of suggestion (the same as the previous one) to the automobile factory through Fujisawa City Office. Then the quality of the river water was restored to the original state.

On October 12, 1962, the intake pump for dilution water stopped suddenly. We disassembled the pump and found two huge eels—about 80 cm. long and weighing about 1 kilogram—and two days later we caught two more rather smaller eels. As the usual size of eels in the Hikichi River is about 20 cm. long, and the night-soil treatment plant had started its operation on February 22, 1961, and its function seemed to be well established around July 1961, it was evident that the eels had grown to that size within a period of 16 months. The reason that the waste did not damage the eels was that sodium cyanide contained in the waste was dispersed into air as a cyanic

**Intake of river water**



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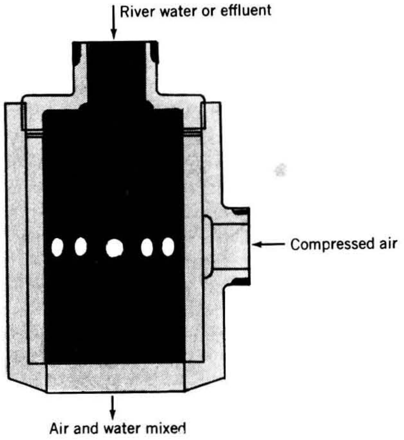
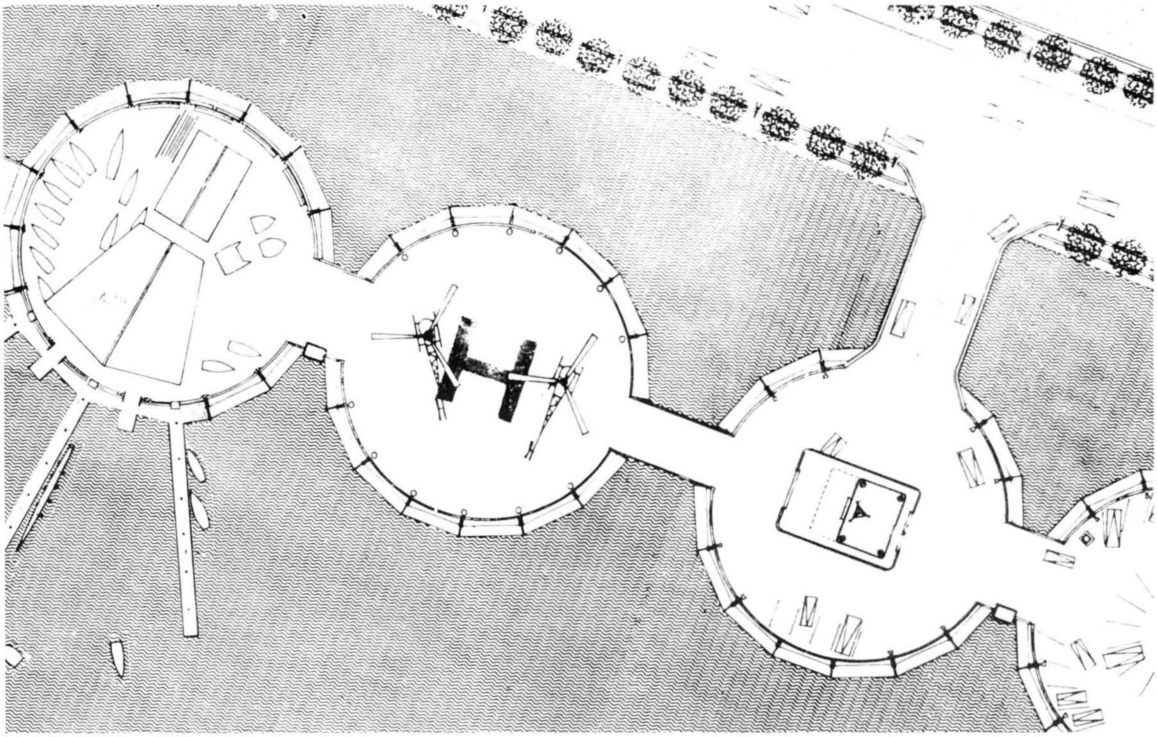


**Shuzo Nishihara** *(deceased) was founder and president of Nishihara Environmental Sanitation Research Corp., Ltd., Tokyo, Japan. Mr. Nishihara was a graduate (1898) in civil engineering of Kohshu Gakko and completed (1904) an English language course at Tokyo School of Foreign Languages. Previously (1917–57), he was founder and president of Nishihara Engineering Works, renamed (1948) Nishihara Engineering Co., Ltd., to which he succeeded as chairman in (1957). From 1899–1915, he held various governmental positions in civil engineering. On several occasions Mr. Nishihara was honored with presentations by the Japanese government for his contributions to sanitation and the development of waste water disposal technology: in 1965 with the Fourth Order of Merit of the Sacred Treasure, in 1956 with the Public Health Award from the Ministry of Welfare, and in 1955 with the Yellow Ribbon Medal. He was a member of the Society of Heating, Air Conditioning, and Sanitary Engineering of Japan, Japan Environmental Sanitation Association, Japan Science Foundation, and Architectural Institute of Japan.*



**Benefits.** Concrete sewage tanks in river offer additional service and recreational areas

acid by the aerative action of the stream, and it did not adversely affect the fishes that live near the bottom of the river.

### Fish growth

I would like to explain here how the effluent from the night-soil high-rate digestion process is effective for the growth of fish. The BOD of night-soil is about 8600-10,000 p.p.m., and it becomes 2600-3000 p.p.m. as a supernatent after high-rate digestion. After being diluted by fresh water and effluent by 15 times, the supernatant receives secondary treatment with a high-rate trickling filter, final settling tank, and chlorination. The BOD of the final effluent is about 30-80 p.p.m. When this effluent is supplied to a pond or a river, it makes the COD of water about 15-20 p.p.m., and has the effect of accelerating the growth of fish. Growth stimulating factors in supernatant are considered to be rich in vitamin $B_{12}$ (15-20 $\mu$g. in dry solids) and other microelements.

I should also like to explain about the condition of marine products in Tokyo Bay and how they are affected by water pollution. In 1938, when Tokyo Bay was in a favorable condition for laver cultivation, annual production of laver was 24,500,000 sheets (size 19.5 cm. × 18 cm., and its present price, 10 yen per single sheet), and its value averaged 245 million yen. Production has been reduced to 180,000 sheets annually in 1963. Fish in Tokyo Bay smell of phenol and are nothing like fish in the old days. Water pollution control is an urgent requirement in this area.

### Plating factories

As I mentioned before, there are many small plating factories and meat processing factories (usually for hogs or poultry), most of them on the scale of domestic industry. And it is very important to provide them with some means of treating their wastes. Otherwise, clarification of the Sumida River will never be realized.

My proposal is to request the metropolitan government to construct four kinds of holding tanks for small plating factories to store their wastes separately as chrome, copper, sulfuric acid, and nitric acid, and collect them separately, by vacuum tank trucks, periodically. When collecting chrome and copper wastes, the vacuum pump will operate in reverse so that it can be used as a compressor and will diffuse cyanic acid into air instantly by aerating the wastes; then wastes will be collected. Collected wastes are carried to treatment plants where chrome waste is treated by electrolysis, copper and zinc wastes by ion exchange, and these metals recovered from the wastes and returned to the original plating factories.

Organic wastes are treated by any suitable high-rate digestion process or high-rate activated sludge process, and recovery of new resources is also considered.

By these methods, I think we can really turn a misfortune into a blessing.

# CURRENT RESEARCH

## Stabilization and Determination of Traces of Silver in Waters

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■ A method has been developed for the determination of silver in water in the parts-per-million to parts-per-billion range. EDTA is employed to stabilize the sample to prevent adsorptive losses of the silver to container walls. Quantitative measurements are made by atomic absorption spectrometry on silver dithizonate complexes after they have been isolated and concentrated into ethyl propionate. The method is specific, convenient, accurate, and widely applicable.

The problem of the determination of trace quantities of silver in waters has engaged the attention of chemists for many years. High priority was assigned to this problem following publication of the 1962 U. S. Public Health Service Drinking Water Standards, which specified a maximum permissible concentration of 0.05 mg. per liter. Chambers and Proctor (1960) provided the first definitive report of the losses of low concentrations of silver to container surfaces. Dagnall and West (1962) also noted significant losses of silver at trace levels. West, West, and Iddings (1966, 1967) indicated that all container materials evaluated adsorbed silver to an alarming degree and that sodium thiosulfate and EDTA were the only effective complexing agents found for keeping the silver in solution. The data indicated a decided preference for sodium thiosulfate for complexation, as less than 1 % silver was adsorbed by any of the container materials studied over a 30-day contact period. The EDTA effectively stabilized the silver for a 10-day holding period with less than 1 % adsorption occurring on any of the five recommended container materials when it was used as the stabilizing agent. Borosilicate glass, polyethylene, silica glass, Teflon, and polystyrene were satisfactory for use with EDTA as the complexing ligand. Flint, silicone-coated materials, polypropylene, and acrylic- and vinyl-coated containers adsorbed excessive quantities of the silver present in the EDTA solution and were not considered satisfactory for use with this ligand.

The objective of the research reported here was to develop an analytical method for the detection and determination of silver in water in the 0.01 to 1.0 mg. per liter range, applicable in the presence of an adequate stabilizing ligand. Atomic absorption spectroscopy was selected as the means of ultimate determination because of its reliability, specificity, speed, and convenience.

### *Experimental*

**Development of Procedure.** The analytical method developed was based on the preferential extraction of silver from the silver-EDTA complex using an ester solution of dithizone (0.05 gram of diphenylthiocarbazone per 100 ml. of ethyl propionate; this solution is stable indefinitely). The ester-dithizone-silver extract was aspirated into an air-acetylene flame for atomic absorption spectrometry. A Perkin-Elmer atomic absorption spectrophotometer, Model 303, with a premixed type acetylene-air burner, Beckman regulator, and silver hollow cathode source, was used. The operating conditions were as follows: wavelength, 3281 A.; lamp current, 14 ma.; slit width, 0.3 mm.; scale amplification not required; flame (oxidizing)—air auxillary, 10 pounds per sq. in., atomizer, 25 pounds per sq. in.; acetylene, 0.55 liter per minute. Minute droplets of water which formed in the solvent layer during the extraction step caused erratic flame characteristics. The addition of 1 ml. of acetone to the 10-ml. ethyl propionate–dithizone-silver fraction following extraction provided a homogeneous solution that yielded very stable and desirable flame characteristics.

EFFICIENCY OF SEPARATION. To determine the efficiency of separation, $Ag^{110}$ was used, and portions of the aqueous and solvent layers were counted in a multichannel analyzer. The extraction coefficient was 19, thus establishing the validity of using only a single extraction in the recommended procedure.

EFFECT OF PH. The effect of pH variation is shown in Table I. Ten milliliters of the samples containing 10 $\mu$g. of Ag were made $0.1M$ with respect to EDTA, extracted with 5 ml. of dithizone–ethyl propionate, and aspirated into the flame under standard conditions. A typical water sample will have a pH of 4.0 to 5.0 after complexation with either 0.1*M* or 0.01*M* EDTA (disodium salt). There were no significant changes in percentage absorption over the pH range of 3.5 to 8.0. However, there was visual evidence of oxidation of the dithizone when the pH exceeded 6.5, and the higher pH range should be avoided if the solvent extracts are to be held for long intervals prior to analysis.

Extract Stability. Preliminary work indicated that the dithizone–ethyl propionate–silver complex was extremely stable following extraction from the aqueous sample. Owing to the initial problems associated with silver losses to contact surfaces, it appeared necessary to observe the extract stability over extended periods of time.

Two samples containing 0.08 mg. per liter of $Ag^{110}$ in 0.1*M* EDTA were carried through the standard separation procedure. The solvent extracts were placed in stoppered borosilicate glass test tubes and held for a two-week period. The tubes were emptied, carefully rinsed, crushed, and the activity levels of the crushed glass counted. There was no detectable increase in the activity of the crushed glass during the two-week exposure to the extracted complex. The extract of the dithizone-silver complex is much more stable than the aqueous solutions of the EDTA-silver complex. However, the dithizone cannot be substituted for EDTA in the initial complexation of the sample or sample preservation, as the EDTA is essential to the sensitivity of the method as well as to the initial sample preservation. Dithizone is not soluble in water and must be introduced via a nonaqueous solvent.

An additional evaluation of the stability of the extract was performed by storing the extract from two samples containing 2 μg. and 20 μg. of Ag, respectively, for a 3-week period. Aliquot portions of the extract were removed periodically for absorption measurements with the atomic absorption spectrophotometer. There was no visual change in the color of the two extracts and no significant change in absorption during the 3-week period (Table II). This stability provides field sampling freedom as samples may be collected, preserved, and extracted and the extracts shipped to base laboratories for subsequent analysis by atomic absorption spectroscopy.

Sensitivity and Precision. The sensitivity of the developed procedure is 0.25 μg. of $Ag^+$ for 1% absorption, or 1.25 p.p.b., without the use of scale expansion. This value was established for the silver extract. Table III summarizes the precision data obtained in the preparation of standard working curves. The working curve is linear between 1 and 30 μg. but exhibits a slight curve between 30 and 50 μg. Owing to the flexibility in sample volume selection permitted by the extraction step, it was most convenient to work in the 1- to 10-μg. range.

Interference Studies. The concentrations for interference studies were selected as representative of contaminant concentrations which might be expected to be found in most applications (Table IV). Gold(III) and surfactant caused low results at high concentrations, but did not interfere with the procedure at concentrations which could reasonably be expected in systems such as mildly polluted or potable waters.

**Table I. pH Range Evaluations**

**10 μg. of $Ag^+$ Added to Each Sample**

| pH | % Absorption | Comment |
|---|---|---|
| 3.0 | 12 | Burner clogging because of heavy precipitate (EDTA) |
| 3.5 | 51 | Clear extract |
| 4.0 | 51 | Clear extract |
| 4.5 | 51 | Clear extract |
| 5.0 | 50 | Clear extract |
| 5.5 | 51 | Clear extract |
| 6.0 | 52 | Clear extract |
| 6.5 | 49 | Extract begins to oxidize |
| 7.0 | 47 | Extract begins to oxidize |
| 8.0 | 52 | Extract begins to oxidize |

**Table II. Stability of the Silver Extract**

| Time Held | % Absorption |
|---|---|
| 2 μg. of $Ag^+$ added, 0.01*M* EDTA | |
| Immediate | 4 |
| 48 hours | 4 |
| 1 week | 4 |
| 2 weeks | 4 |
| 3 weeks | 3 |
| 20 μg. of $Ag^+$ added, 0.01*M* EDTA | |
| Immediate | 32 |
| 48 hours | 32 |
| 1 week | 31 |
| 2 weeks | 31 |
| 3 weeks | 25 |

**Table III. Precision Data from Standard Curves**

| $Ag^+$ Added, μg. | Number of Determinations | Standard Deviation, μg. (95% Confidence Level) |
|---|---|---|
| 1.0 | 14 | 0.02 |
| 3.0 | 5 | 0.00 |
| 5.0 | 14 | 0.01 |
| 7.0 | 5 | 0.02 |
| 10.0 | 14 | 0.02 |

100-ml. sample extracted with 10 ml. of ethyl propionate–dithizone solution.

Variation of the EDTA Concentration. In the surface adsorption studies conducted by West, West, and Iddings (1966, 1967), all work evaluating the effectiveness of EDTA as a complexing ligand was conducted at the 0.1*M* concentration. This approaches the solubility limit for EDTA in water. As it is difficult to dissolve 4 grams of EDTA in 100 ml. of water sample under field conditions, it became necessary to evaluate the effectiveness of lower concentrations of EDTA for complexation purposes. Cost and bulk of the higher EDTA concentration were also of importance. Decreasing the EDTA concentration from 0.1*M* to 0.01*M* had no effect on the efficiency of extraction nor on the absorbance readings over the entire range of the standard curve, nor did it alter the stability of the solvent complex.

New borosilicate glass beakers, from random lots, were used to check the inhibition of adsorption by the lower EDTA concentration, and the tracer techniques employed in the 1966 and 1967 studies were used. After a 2-week holding period, all samples were found to have remained stable. Adsorption losses were less than 1% in all cases. In contrast

Table IV. Interference Studies

| Group | Concentration, Mg./Liter | Comments |
|---|---|---|
| I. $Cu^{+2}$, $Li^{+}$, $Na^{+}$, $K^{+}$ | 500 | No interference[a] |
| Au(III) | 10 | Results 67% low |
| | 1 | No interference |
| II. $Be^{+2}$, $Zn^{+2}$, $Cd^{+2}$, $Mg^{+2}$, $Ca^{+2}$, $Sr^{+2}$, and $Ba^{+2}$ | 500 | No interference |
| $Hg^{+2}$ | 100 | No interference |
| III. $Bo_2^{-}$, $B_4O_7^{-2}$, $Al^{+3}$, $Ce^{+3}$ $Tl^{+}$ | 500 | No interference |
| IV. $CO_3^{-}$, Zr(IV), Sn(IV), $Pb^{+2}$ | 500 | No interference |
| $SiO_3^{-2}$ | 500 | Low results |
| | 100 | No interference |
| V. $NH_4^{+}$, $NO_3^{-}$, $HPO_4^{-2}$ | 500 | No interference |
| $Sb^{+5}$, $HAsO_4^{-2}$, $VO_3^{-}$ | 100 | No interference |
| Bi(V) | 10 | No interference |
| VI. $SeO_3^{-2}$, $Cr_2O_7^{-2}$, $TeO_3^{-2}$, $MoO_4^{-2}$, $WO_4^{-2}$, $UO_2^{+2}$ | 500 | No interference |
| VII. $F^{-}$, $Cl^{-}$, $Br^{-}$, $I^{-}$, $Mn^{+2}$ | 500 | No interference |
| VIII. $Fe^{+3}$, Pd(II) | 100 | No interference |
| Miscellaneous, tartaric, oxalic, citric, tannic acids | 500 | No interference |
| $Cl_2$ | 5 | No interference |
| Surfactant(ABS) | 10 | Low results |
| | 2 | No interference |

[a] Less than 1 p.p.b.

to the adsorption data obtained in the earlier studies with traces of NaCl in $Na_2S_2O_3$ solution, traces of NaCl in the EDTA system (both 0.1 and 0.01*M*) actually further inhibited surface adsorption.

The continued increase in adsorption by the container materials beyond a 10-day to 2-week contact period, with both 0.1*M* and 0.01*M* EDTA, and the irregular adsorption characteristics of various container materials noted in earlier studies restrict safe sample storage or holding intervals to 10 days. As noted earlier, container materials should be restricted to borosilicate glass, polyethylene, silica glass, Teflon, and polystyrene.

**Procedure.** Sample Preservation. Sufficient dry disodium salt of EDTA should be added to the water sample at the time of sample collection to provide approximately 0.01*M* solution with respect to EDTA. For example, a 100-ml. water sample would require the addition of 0.4 gram of EDTA. The sample should be analyzed within 10 days following collection to avoid breakdown of the complex and the silver becoming lost to the container surfaces.

Following addition of the EDTA, a typical water sample will have a pH of 4.0 to 5.0. The optimum pH range for this method is 3.5 to 6.5. Either dilute $HNO_3$ or dilute $NH_4OH$ may be added if necessary for pH adjustment just prior to the extraction step.

Extraction of Silver. An appropriate volume of sample treated as noted above, is added to a separatory funnel. For waters containing 0.005 to 0.05 mg. per liter of silver, a 200-

ml. volume is required. For the 0.01 to 0.10 mg. per liter range, 100 ml., or for the 0.10 to 1.0 mg. per liter range, 10 ml. of sample are required. Ten milliliters of the dithizone–ethyl propionate reagent are added. The sample is shaken with short rapid strokes for 1 minute. Approximately 10 minutes should be allowed for adequate separation of the aqueous and solvent phases. The aqueous phase is drained to waste. The stem end of the separatory funnel is wiped dry, as the presence of moisture is critical. The solvent is then released into a dry test tube provided with a tight inert stopper. One milliliter of acetone is added to the sample extract in the test tube to eliminate problems caused by any remaining minute droplets of water entrapped in the solvent.

STANDARD SERIES. A standard working curve is prepared by adding suitable aliquots of the standard silver solution to separatory funnels and diluting to the volume required by the sample concentration range with $0.01M$ EDTA as discussed above under the extraction step. The silver stock solution is prepared by dissolving 0.0787 gram of $AgNO_3$ and diluting to 500 ml. with silver-free distilled water. This stock solution must be prepared fresh. One milliliter = 100 μg. of silver. The standard silver solution is prepared by diluting 1 ml. of stock silver solution to 100 ml. with $0.01M$ EDTA solution. The $0.01M$ EDTA solution is prepared by dissolving 3.72 grams of the disodium salt of EDTA and diluting to 1 liter with silver-free distilled water.

These standards are carried through the extraction step along with the samples. Standards containing 1, 3, 5, 7, and 10 μg. of silver give a straight-line curve when absorbance values are plotted against micrograms of silver. The solvent extract is stable for 3 weeks.

CALCULATIONS. After the samples have been introduced into the flame and absorbance values obtained, the micrograms of silver present are determined from the standard curve.

$$\mu\text{g./liter} = \mu\text{g. of Ag}^+ \times \frac{1000}{\text{ml. of sample}} \quad (1)$$

$$\text{mg./liter} = \frac{\mu\text{g. of Ag}^+ \text{ found in sample}}{\text{ml. of sample}} \quad (2)$$

### *Results and Discussion*

The silver-thiosulfate complex was studied first because of its superior stability. West, West, and Iddings (1966, 1967) showed that with even trace amounts of NaCl present, it was necessary to use $1.0M$ rather than $0.1M$ $Na_2S_2O_3$ to prevent adsorption, and all work performed with thiosulfate was at this higher concentration. The various approaches tried and the conclusions reached are summarized below.

**Direct Aspiration of Sample.** This did not provide adequate sensitivity for the range of interest. Only moderately good results were obtained at the 1.0 mg. per liter of silver concentration. Frequent burner clogging, owing to the high salt concentration of the $1.0M$ $Na_2S_2O_3$, was encountered.

**Use of a T-Piece.** The use of a quartz T-piece over the Beckman total consumption burner was abandoned because of serious clogging of the burner and because the background due to the thiosulfate was too high to permit desired sensitivity.

**Preheated Burner.** The new Beckman preheated burner was used. This produced excellent results, but after each 1 or 2 minutes of operation, the preheated chamber had to be dismantled and cleaned because of deposition of solids.

**Addition of Enhancing Reagents.** Previous work with other metals indicated that small amounts of various reagents may provide enhancement of the absorption signal, thus extending sensitivity ranges severalfold. The enhancement trials were made using dithizone dissolved in acetone, isopropyl alcohol, methyl ethyl ketone, diethylene glycol, propylene glycol, ethylene glycol monoethyl ether, nitrobenzene, and ethylenediamine. Similar trials were made using dithiooxamide dissolved in these solvents. No substantial enhancement was obtained in any case.

Work was abandoned with the silver-thiosulfate complex as the complex proved to be extremely stable in the flame. This stability prevented the production of sufficient silver atoms in the flame, thus adequate sensitivity could not be obtained.

**Studies of the EDTA Complex.** An acetylene-air flame produced the best sensitivity for the silver-EDTA complex. As a concentration of 0.10 mg. per liter of silver in $0.1M$ EDTA solution aspirated directly into the air-acetylene flame produced no absorption, either an enhancing agent or a prior concentration step, or both, would be necessary. It was encouraging that there were no burner clogging problems or high background signals due to the $0.1M$ EDTA solution. However, the addition of such possible enhancing reagents as rubeanic acid, diethylene glycol, ethanol, or isopropyl alcohol or extraction as dithizonate in carbon tetrachloride, methyl isobutyl ketone, or kerosine was of no value.

The effect of concentrating the silver from water samples, dosed to contain $0.1M$ EDTA was evaluated. Dithizone in petroleum ether, butyl ether, 1-nitropropane, and in ethyl propionate was added to the samples, extracted for 1 minute with a single separation, and the extracts were aspirated directly to the air-acetylene flame. The solvent extracts from the dithizone–ethyl propionate addition provided very sensitive and reproducible results. The analytical method developed utilized a separation employing this reagent combination. The customary solvents for dithizone, such as chloroform or carbon tetrachloride, could not be used as they decomposed in the flame to produce phosgene and also produced erratic flame characteristics. Two additional esters were evaluated for comparison with the ethyl propionate–dithizone combination. Ethyl benzoate was too soluble in the EDTA system. *n*-Propyl propionate gave a clear, sharp separation between the solvent and aqueous phase but failed to provide adequate sensitivity.

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# Determination of Calcium in Natural Water by Atomic Absorption Spectrophotometry

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■ The determination of calcium in natural waters by atomic absorption spectrophotometry (AAS) is highly pH dependent. The response of the AAS for a constant calcium concentration in natural water increased with decreasing pH in the range of pH 7.0 to 3.8. It was constant in the pH range of 3.8 to 1.8 and decreased with decreasing pH below 1.8. Correct analyses were obtained when samples were adjusted to pH 1.8 to 3.8. The pH effect on calcium response above pH 3.8 is due to bicarbonate. Calcium carbonate precipitation occurs in the burner and causes the low response. In addition to pH adjustment, the addition of 50% of the EDTA required to titrate the hardness of the water or the addition of 1% lanthanum will eliminate the pH dependence of calcium response.

Since water samples are routinely analyzed for calcium, a quick, accurate, and precise analytical procedure is desirable. Analytical procedures currently employed for the determination of calcium are EDTA titration, precipitation, and weighing of calcium oxalate, redissolving precipitated calcium oxalate and titrating with permanganate, flame photometry, and atomic absorption spectrophotometry. The atomic absorption spectrophotometric method of analysis for calcium compares favorably with other methods (West and Herrin, 1965). Some of the problems encountered with other methods of analysis, such as difficulty in determining colorimetric end points, the large sample volumes required, and interferences from other elements, are not encountered in the atomic absorption spectrophotometric procedure (Butler and Drink, 1963). The literature on the use of atomic absorption spectrophotometry for water analysis has been reviewed (Bentley, 1967).

An atomic absorption spectrophotometer is currently utilized for calcium analysis of lake, stream, and river water samples in this laboratory. The procedure is quick, accurate, and precise; however, some problems have been encountered. The apparent calcium concentration obtained by this procedure is pH dependent—i.e., as the pH is varied, the apparent calcium concentration varies. This paper presents the results of a study to determine why the apparent calcium concentration obtained by this procedure is pH dependent.

### *Experimental*

Calcium analyses were performed using a Perkin-Elmer atomic absorption spectrophotometer, Model 303. Measurements were made at a wavelength of 4227 A. and a slit setting of 4. The visible range was used and the source current was set at 14 ma. A scale setting of 1 and an air flow rate of 5 flowrater units was employed. Before the start of each series of analyses, the gas (acetylene) flow rate was adjusted to give maximum absorbance while aspirating a standard solution. This value was usually 9.5 flowrater units. The aspiration rate was checked by using a stopwatch and graduated cylinder. Plugging of the aspirator was not excessive and, when it occurred, was rectified by aspirating 1 to 1 hydrochloric acid for 1 minute.

A Beckman pH meter, Model GS, was used to make pH measurements on each sample before determination of calcium. Each sample was kept in a covered volumetric flask between the time of preparation and the time of analysis.

Sodium, potassium, and magnesium were determined with the atomic absorption spectrophotometer utilizing the manufacturer's recommended instrument settings (Perkin-Elmer Corp., 1966).

Reagent grade chemicals were used to prepare all solutions utilized in the experimental work.

Unless otherwise specified, sample refers to Lake Mendota water samples which were obtained from the Water Chemistry Laboratory lake water tap. This system provides untreated lake water from approximately 600 feet offshore from a depth of about 10 feet below the surface. Samples from other lakes were obtained on field trips and stored in polyethylene bottles at 5° C. All samples were filtered with a Whatman No. 1 paper, and glass-distilled water was used to prepare dilutions, as well as to zero the atomic absorption spectrophotometer.

Synthetic lake water was prepared by weighing and diluting with glass-distilled water, chemicals in sufficient quantities to give values of elements comparable to those found in Lake Mendota (Lee, 1966). This solution was used in the deter-

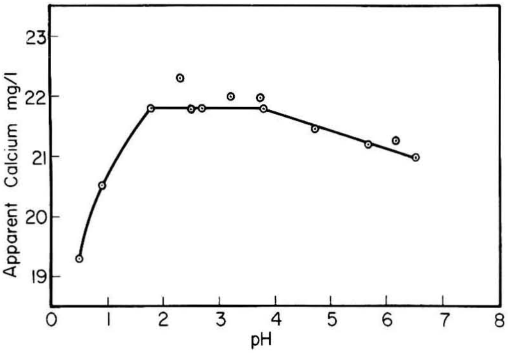

**Figure 1. Effect of pH on apparent calcium concentration of Lake Mendota water**

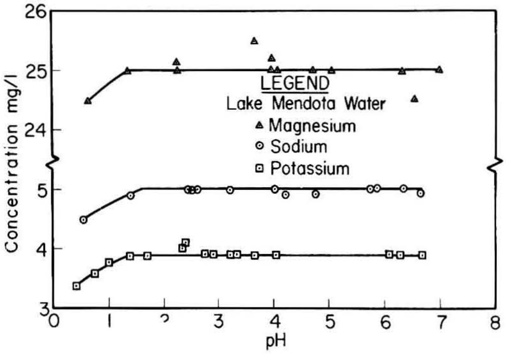

**Figure 2. Effect of pH on apparent magnesium, sodium, and potassium concentration in Lake Mendota waters**

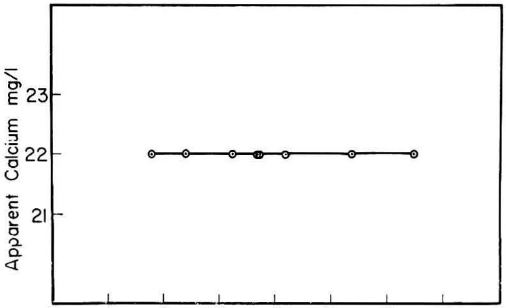

**Figure 3. Effect of pH on calcium analyses in synthetic Lake Mendota water with organic matter or dextrose**

**Table I. Apparent Calcium Concentration at Normal and Low pH**

| | Calcium Mg./Liter | |
|---|---|---|
| Sample Source | Without acid | pH adjusted to 2.4 |
| Black Earth Creek | 49.0 | 52.0 |
| Comstock Lake | 19.1 | 23.5 |
| Big Twin Lake | 21.5 | 23.0 |
| Fox Lake | 31.3 | 38.8 |
| Lake Katrine | 6.0 | 5.3 |

mination of the effect of organic material on the pH-calcium relationship.

Organic material was obtained by evaporation concentration of Lake Mendota water and placement of the concentrate on a Sephadex G-75 column. Separation of the sample, by molecular weight, was achieved and the high molecular weight, low conductance fraction was used in this study (Gjessing and Lee, 1967). The total hardness and alkalinity analyses were performed by Standard Methods (APHA 1965) procedures.

*Results*

A linear relationship was found for standard calcium solutions in the 1 to 10 mg. per liter range. All samples were diluted to obtain calcium concentrations in this range. The standard deviation of this analysis was ±0.5 mg. per liter, at the 95% confidence level.

Figure 1 is typical of the results obtained when samples are acidified and diluted 5 to 1, pH is measured, and calcium analyses are performed on a sample of Lake Mendota water. The apparent calcium concentration is constant in the pH range 1.8 to 3.8. Above pH 3.8, it decreases with increasing pH and, below pH 1.8, decreases with decreasing pH. These results show the pH range, in which the apparent calcium concentration is constant, to be approximately 2.0 pH units. A similar variation in apparent calcium concentration with pH was observed for other lake, stream, and river samples. Table I gives the results of determining apparent calcium at the original pH of the samples and at pH 2.4. The error that may be involved in the determination of calcium with atomic absorption, without pH adjustment, can be seen. For example, a Fox Lake sample had 38.8 mg. per liter of calcium; however, only 31.3 mg. per liter was found by atomic absorption analysis without acidification.

Experiments were run to determine if the apparent concentrations of sodium, potassium, and magnesium, as determined by atomic absorption, were pH dependent. Figure 2 shows that the apparent concentration of these elements is not affected by changes in pH above 1.8, but decreasing pH below this value caused a decrease in apparent concentration. These results indicated that the cause of variation in apparent calcium above pH 3.8 was not due to some instrumental parameter, as it would have been found in the determination of magnesium, sodium, and potassium. Below pH 1.8, the variation could be the result of a change in an instrumental parameter since all four elements showed a similar pH dependence

In an effort to determine the cause of the pH dependence on calcium analyses above pH 3.8, studies were made on the effect of organic matter and alkalinity on calcium response in atomic absorption analyses.

Series of experiments were run to determine the effect of organic material on the pH-calcium relationship. In the first series, dextrose was used as the source of organic material in preparing synthetic lake water. Material separated on a Sephadex column, after evaporation concentration, was used as the source of organic material in the next series of analyses. Figure 3 is typical of the results obtained for synthetic water devoid of bicarbonate alkalinity and containing dextrose or organic material. This material had no effect on the apparent calcium concentration from pH 1.8 to 6.5.

A sample of Lake Mendota water was used to determine the effect of the type of alkalinity on the calcium-pH relationship. The alkalinity of Lake Mendota is 140 to 149 mg. per liter as $CaCO_3$. As can be seen, the original Lake Mendota water, in which essentially all of the alkalinity is bicarbonate, showed a similar pH-calcium relationship (Figure 1). A sample of this water was treated with concentrated hydrochloric acid to remove all carbonic species. Concentrated ammonium hydroxide was added to restore the alkalinity and pH to their original values. Calcium measurements were made at various pH's on this water (hydroxide alkalinity curve, Figure 4). The apparent calcium is independent of pH in this sample. The sample was then treated with concentrated hydrochloric acid to remove the hydroxide alkalinity. Sodium bicarbonate was added to this water to increase the alkalinity to its original value, and calcium analyses, as a function of pH, were made on the solution (bicarbonate alkalinity curve, Figure 4). The addition of bicarbonate to this sample resulted in a similar calcium-pH relationship, as was found in the original untreated water. The amount of calcium present in the sample was different after each treatment because of the dilution of the sample by the addition of various reagents. These results indicate that the bicarbonate system is, in some manner, responsible for the low results obtained when the pH is above 3.8. Calculations based on solubility data do not indicate the possibility of calcium carbonate precipitation at pH 4.0 and that a sample containing 21.0 mg. per liter calcium must have its pH raised above 8.3 before carbonate precipitation will occur. These calculations, and the experienced lowering of apparent calcium content at pH 4.0, make it appear that the pH of the sample is being raised to a higher value between the time of aspiration and the time it reaches the flame.

To determine if the pH of the sample was being raised in the aspiration system, a 20% excess of the volume of EDTA required to titrate total hardness was added to the samples. Figure 5 shows apparent calcium to be constant in the pH range 1.8 to 7.9, and that essentially all of the calcium in a sample, with a measured injection pH of 4.0, is evidently complexed with EDTA when aspirated into the flame. As little as 50%, and as much as 200%, of the amount of EDTA needed to titrate total hardness of samples, allows the determination of the same apparent calcium concentration. Table II compares the results of the analysis of water from four different lakes on which 50% of the EDTA required to titrate their hardness was used or the pH of the sample was

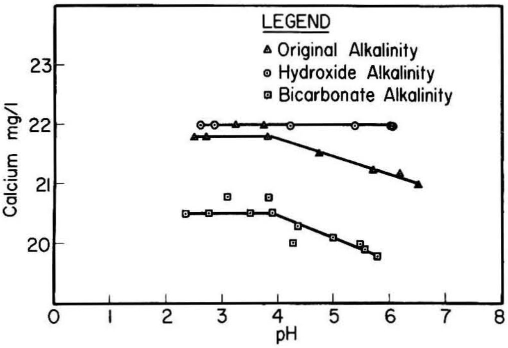

Figure 4. Effect of pH and bicarbonate or hydroxide alkalinity on apparent calcium concentration in Lake Mendota water

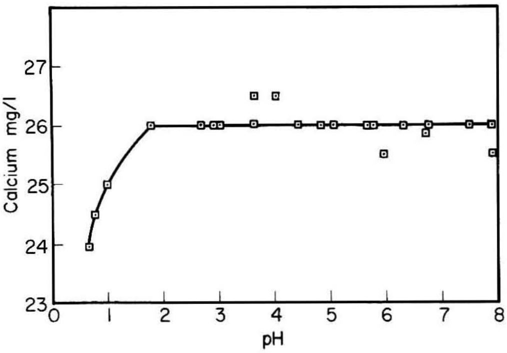

Figure 5. Effect of pH on apparent calcium concentration in Lake Mendota with 20% excess EDTA over that needed to titrate hardness

**Table II. Comparison of Apparent Calcium Concentrations in Lake Waters**

| Sample Source | Calcium, Mg./Liter<br>With 50% EDTA | <br>Without EDTA | <br>pH 2.4 |
|---|---|---|---|
| Fox Lake | 39.5 | 33.5 | 40.0 |
| Cox Hollow Lake | 26.0 | 22.0 | 26.5 |
| Parker Lake | 19.0 | 16.0 | 19.5 |
| Lake Mendota | 26.0 | 23.5 | 26.0 |

adjusted to 2.4. Both pretreatments yielded essentially the same result.

The decreased apparent concentration of calcium, magnesium, sodium, and potassium, at pH less than 1.8, must be due to properties of the instrument or aspiration system, since approximately equal effects were noted with each element. An increase in viscosity might have caused the observed results. However, measured changes in viscosity, as a function of pH on these samples, could not account for the marked apparent concentration-pH relationships observed based on the results of Winefordner and Latz (1961) and Zaugg and Knox (1966). Therefore, at this time, the effect of pH on apparent concentrations of pH below 1.8 cannot be explained.

Lanthanum chloride is routinely used in the determination of calcium by atomic absorption spectrophotometry (Perkin-Elmer Corp., 1966) and will eliminate interferences due to phosphate, sulfate, and bicarbonate (Fishman, 1966). Results obtained by the addition of 1% lanthanum and by pH adjustment are shown in Table III. The results agree within the experimental error of this procedure (±0.5 mg. per liter) on all of the samples, except Lake Mendota. To determine if sulfate or phosphate was causing the difference observed on Lake Mendota water, each compound was added separately to calcium standard solutions and their absorbances were determined. Phosphate, when added in excess of that found in Lake Mendota, caused no change in absorbance by the calcium solution, but sulfate at 20 mg. per liter caused a decrease in absorbance of approximately 4%. Sulfate could be responsible for the difference observed in Lake Mendota water because a 4% change would cause a difference of approximately 1.0 mg. per liter in a sample containing 20.0 mg. per liter calcium. Further study is needed to elucidate the difference.

### *Discussion*

The apparent calcium concentration of water samples, containing bicarbonate alkalinity, is pH dependent. It is constant in the pH range 1.8 to 3.8 and samples must have their pH adjusted to this range before analysis. This is a more stringent pH requirement for calcium analysis than reported by Fishman (1966), who states that pH must be less than 7.0 to obtain good results.

**Table III. Calcium Values Obtained at pH 2.4 and with 1% Lanthanum**

| Samples | Calcium, Mg./Liter<br>pH 2.4 | <br>1% Lanthanum |
|---|---|---|
| Little Cedar Lake | 30.0 | 30.0 |
| Cox Hollow Lake | 23.5 | 24.0 |
| Lake Redstone | 26.0 | 25.5 |
| Lake Mendota | 27.0 | 28.0 |

Results indicate precipitation of calcium carbonate may be responsible for the low values obtained when a sample, with a measured pH greater than 4, is aspirated. The pH of the sample would have to be raised within the sampling system to a value greater than 8.3. The experiments with EDTA tend to support that this is happening, because at pH 7, approximately one half the calcium in a sample is complexed with EDTA (Welcher, 1958). Results show that an appreciable amount of calcium is complexed when a sample, with a measured pH of 4.0, is aspirated into the flame. The increased temperature in the burner head and reduced pressure in the aspiration system could cause carbon dioxide to pass out of solution, increasing the pH. Ramakrishna, Robinson, *et al.* (1966) found that $CO_3^{-2}$ at 100 p.p.m. caused an interference in $Ca^{+2}$ determination. They did not report any pH effect on analysis. They found that the addition of EDTA and $SrCl_2$ tended to remove this interference.

The decrease in apparent concentration obtained below pH 1.8 is due, in part, to increasing viscosity with decreasing pH. A decrease in viscosity causes less sample to be aspirated per unit time, thereby causing a decrease in observed apparent concentration.

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# Geochemistry of Some Tertiary and Cretaceous Age Oil-Bearing Formation Waters

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■ This research was done to interpret the relationships of ions dissolved in some oil-bearing Mississippi and Alabama formation waters, the relationships to their environment, and their origin. The waters were analyzed by published methods developed by the Bureau of Mines. Sodium, calcium, magnesium, chloride, bromide, iodide, bicarbonate, and sulfate ions were investigated. The age of water-bearing rock, the association of all samples with petroleum, and the depth of water-bearing rock were known environmental conditions. The data were analyzed using a digital computer factor analysis program. Correlations were found for several ions and for some ions and their environment. The bromide ion provided a means to distinguish the Tertiary age waters (low bromide concentration) from the Cretaceous age waters (relatively high bromide concentration).

Oilfield waters obtained from marine rocks usually are relict sea water. Their salinity ranges from 35 parts per thousand to more than 300 parts per thousand.

The samples were procured from primary production oil wells. Care was taken to assure that the samples were not contaminated by intrusion of water from other formations. Age of the well, type of completion, and history of brine and crude oil production were other selection criteria. Samples were not taken from recently completed oil wells because of possible drilling fluid contamination. Water produced from gas fields was not sampled because of possible condensed water contamination by dilution.

The samples were analyzed for calcium, magnesium, bicarbonate, sulfate, chloride, bromide, and iodide (A.P.I., 1965; Collins, Pearson, *et al.*, 1961). Sodium was calculated by subtracting the milliequivalents of determined cations from the milliequivalents of determined anions. This does not produce a true sodium value but represents mainly sodium plus potassium.

The approximate geographic location of each sample plus the oilfield, geologic formation, depth, specific gravity, resistivity, and milligrams per liter of calcium, magnesium, sodium, barium-strontium, bicarbonate, sulfate, chloride, and total dissolved solids for each sample were published (Hawkins, Jones, *et al.*, 1963). The concentration of bromide and iodide for 280 of the samples was published (Collins, Zelinski, *et al.*, 1967).

### *Classification of Waters*

Ground waters are classified according to kinds of constituents dissolved in them. Of the more important inorganic constituents which are useful in such classifications, this paper is concerned with sodium, magnesium, calcium, chloride, bromide, sulfate, and bicarbonate.

Table I illustrates five types of waters containing the major ions chloride, bromide, sulfate, bicarbonate, sodium plus potassium, calcium, and magnesium.

Sulfur may be present in oilfield brines with low *Eh* (redox potential) values in the form of thiosulfate rather than sulfate. Some of our field tests indicate this (Collins and Egleson, 1967).

The $HCO_3$-Na and $SO_4$-Na water types shown in Table I are characteristic of artesian waters. The third water is normal sea water. The fourth water, a Cl-Mg type, is characteristic of waters associated with evaporites. It is relict sea water which was concentrated by evaporation and is depleted in calcium, sulfate, and bicarbonate. The fifth water, Cl-Ca type, is characteristic of a very old stagnant water. It is associated with diagenetic dolomitization. Also, this water might be classified as an altered bittern, because the bromide content is higher than a normal evaporite associated water.

In addition to the waters shown in Table I, there are several possible intermediate type waters. For example, some relict sea waters contain more bromide than can be concentrated during evaporite formations. This type of water could be associated with bromide concentrators such as seaweeds, corals, etc.

Some waters contain less bromide than evaporite associated waters. A water of this type contains dissolved halite or has been diluted with meteoric water.

### *Tertiary and Cretaceous Waters*

The Alabama and Mississippi Tertiary and Cretaceous waters evaluated can be classified as Cl-Ca type waters. However, they are two distinct types of Cl-Ca waters. The Tertiary waters probably contain dissolved halite, possibly because they contain less bromide than a normal evaporite associated water, as illustrated in Figure 1.

The Cretaceous waters all contain more bromide than normal evaporite associated waters (Figure 1). This additional bromide could have been added to the waters during diagenesis. Another possibility is that significant amounts of other ions were removed by halmyrolysis.

**Correlation Coefficients.** The correlation matrix, which gives correlations among variables, was obtained using a digital

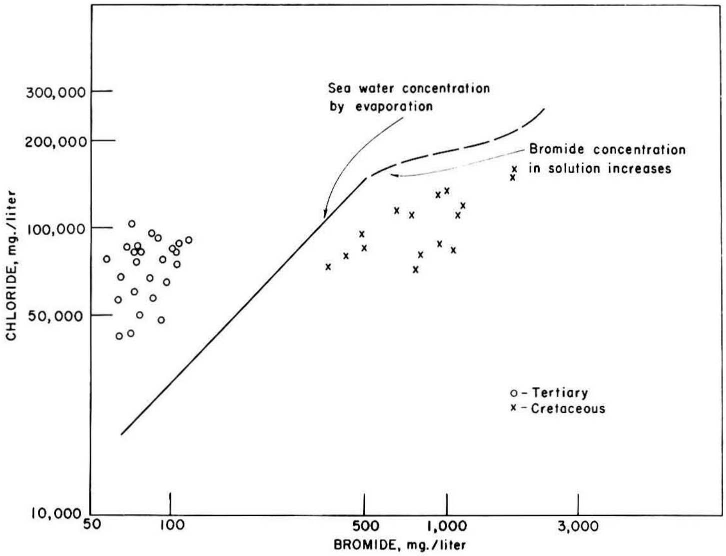

**Figure 1. Bromide *vs.* chloride for some representative Mississippi and Alabama Tertiary and Cretaceous oilfield brines**

computer. The 10 variables shown in Table II can be regarded as points plotted in a hyperspace. The correlation coefficients are the cosines of the angles between vectors connecting the points with the origin.

The correlation coefficient matrix is a measure of how well the variance of each constituent can be interpreted by relationships with each of the other constituents. For example, in Table II, column 6, row 2, the value 0.965 is a measure of the degree to which the variation in concentration of chloride is associated with variation in concentration of total dissolved solids. The number 0.965 indicates that there is a high degree of mutual association, because the closer the coefficient approaches +1.00 or −1.00, the higher the degree of interrelation. There were 268 samples, both Tertiary and Cretaceous, subjected to the analysis shown in Table II.

The correlation coefficient matrix for 142 Tertiary age samples is shown in Table III. The degrees of correlation obtained for the Tertiary age samples are somewhat different than the combined data correlations. The correlation coefficient matrix for 126 Cretaceous samples is shown in Table IV. Obviously, there are higher degrees of relationships between more ions in the Cretaceous age waters than in the Tertiary age waters. The variances between Table II and Tables III and IV are affected not only by the data but also by the degrees of freedom.

Plots of any two variables—i.e., Cl *vs.* T.D.S.—which have correlation coefficients greater than 0.7 will be nearly linear. The more interesting high degrees of correlation are Ca-Br, Ca-depth, and Cl-Br. The first two are indicative of old stagnant waters associated with diagenetic dolomitization. The third Cl-Br, found only for the Cretaceous age waters, is significant because it shows a definite relationship of Cl to Br in the Cretaceous age waters.

**Low Correlation.** Iodide, bicarbonate, and sulfate do not correlate with any other variable. The bicarbonate analysis is suspect unless the water is analyzed immediately when sampled. This was not done and could be the reason why bicarbonate does not correlate.

The sulfate analysis was accurate to ±8% of the amount present. Most of the Tertiary samples contained no sulfate, and this is one reason why it did not correlate.

The iodide analysis was accurate to ±10% of the amount present. A factor which can affect iodide abundance in ground waters is an ionization potential of 2.16 which indicates it is not likely to remain in true ionic solution. The oxidation potential indicates that only iodate is thermodynamically stable (Sillén, 1961). Most oilfield waters have low *Eh* values, indicating a reducing environment. Therefore, the iodate may be reduced to iodine and lost by volatilization, or it may be depleted in an area by ion exchange or halmyrolysis and dissolved in another area.

The geochemistry of iodine obviously is complex. Figure 2 illustrates the amount of iodide concentration that can be expected by normal evaporation of sea water. All oilfield waters that the author has examined contain more iodide than can be charged to this concentration mechanism.

Magnesium in general did not correlate well. In the total data correlation shown in Table II, a coefficient of 0.724 is shown for Mg-Br. The Tertiary samples gave a low Mg-Br correlation of 0.222. The Cretaceous samples gave a 0.533 correlation. The relatively high coefficient for the total data correlation could be attributed to the additional degrees of freedom.

### *Bromide Concentration*

Bromide does not form its own minerals when sea water evaporates. It forms an isomorphous admixture with chloride in the precipitates (Valyashko, 1956; Braitsch and Herrmann, 1963). As sea water evaporates, the carbonates precipitate

**Table I. Types of Waters**

| No. | Concentrations in Mg. per Liter |  |  |  |  |  |  | Type |
|---|---|---|---|---|---|---|---|---|
|  | Na | Ca | Mg | Cl | Br | $SO_4$ | $HCO_3$ |  |
| 1 | 1,600 | 40 | 40 | 820 | 10 | 340 | 2800 | $HCO_3$-Na |
| 2 | 1,100 | 280 | 75 | 560 | 8 | 2200 | 420 | $SO_4$-Na |
| 3 | 10,600 | 900 | 1300 | 19,000 | 65 | 3900 | 160 | Sea water |
| 4 | 23,000 | 1,000 | 4000 | 36,000 | 118 | 1000 | 80 | Cl-Mg |
| 5 | 18,700 | 120,000 | 9000 | 270,000 | 3200 | 0 | 0 | Cl-Ca |

**Table II. Correlation Coefficients, All Samples**

|  | Depth | T.D.S. | Na | Ca | Mg | Cl | Br | I | $HCO_3$ | $SO_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Depth | 1.000 | 0.793 | 0.473 | 0.767 | 0.477 | 0.763 | 0.631 | 0.562 | −0.387 | 0.329 |
| T.D.S. | 0.793 | 1.000 | 0.771 | 0.781 | 0.566 | 0.965 | 0.704 | 0.279 | −0.402 | 0.277 |
| Na | 0.473 | 0.771 | 1.000 | 0.219 | 0.151 | 0.727 | 0.187 | −0.026 | −0.046 | 0.184 |
| Ca | 0.767 | 0.781 | 0.219 | 1.000 | 0.657 | 0.760 | 0.890 | 0.474 | −0.560 | 0.245 |
| Mg | 0.477 | 0.566 | 0.151 | 0.657 | 1.000 | 0.571 | 0.724 | 0.256 | −0.464 | 0.089 |
| Cl | 0.763 | 0.965 | 0.727 | 0.760 | 0.571 | 1.000 | 0.681 | 0.271 | −0.404 | 0.261 |
| Br | 0.631 | 0.704 | 0.187 | 0.890 | 0.724 | 0.681 | 1.000 | 0.435 | −0.568 | 0.209 |
| I | 0.562 | 0.279 | −0.026 | 0.474 | 0.256 | 0.271 | 0.435 | 1.000 | −0.343 | 0.217 |
| $HCO_3$ | −0.387 | −0.402 | −0.046 | −0.560 | −0.464 | −0.404 | −0.568 | −0.343 | 1.000 | −0.004 |
| $SO_4$ | 0.329 | 0.277 | 0.184 | 0.245 | 0.089 | 0.261 | 0.209 | 0.217 | −0.004 | 1.000 |

first, followed by the sulfates. Little or no bromide precipitates or is occluded with these.

Halite (NaCl) begins to precipitate when the chloride concentration is about 137,000 mg. per liter compared with that of normal sea water, 19,000 mg. per liter. Some bromide is entrained with chloride in the precipitate. However, with each crystallization, more bromide is left in solution that is entrained in the precipitate.

Sylvite (KCl) begins to precipitate when the chloride concentration is about 158,000 mg. per liter, followed by Carnallite $MgCl_2 \cdot KCl \cdot 6H_2O$ at 172,000 mg. per liter and Bischoffite $MgCl_2 \cdot 6H_2O$ at 198,000 mg. per liter. At each eutectic point, the concentration rate of bromide in solution increases. The change in slope in Figure 1 illustrates this approximately.

Other concentration mechanisms must operate to account for the high bromide concentrations, 6000 mg. per liter, found in some brines. The data in Figure 1 only allow about 2500 mg. per liter of bromide in a very concentrated brine.

Primary evaporite formation could occur in a lagoon or similar area where the lagoon became closed to the sea. Secondary evaporite formation could occur after a later geologic occurrence which allowed new sea water to inundate the lagoon. The diluted evaporite associated water would have a bromide content greater than that of normal sea water. If the lagoon again became closed to the sea, a secondary evaporite could form. Eustatic occurrences could account for waters containing high bromide concentrations.

Other possible concentration mechanisms are relict sea water that contained more bromide than modern sea water, dissolution of minerals containing high concentrations of bromide by sea water, dilution of concentrated brines by sea water, and an abundance of bromide concentrators, such as the seaweed *Desmaresta* or the coral *Gorgonellidae* (Vinogradov, 1953) which released bromide to the sea water.

The Tertiary samples contained less bromide than can be attributed to sea water evaporation. They either were diluted with meteoric water or were diluted and contained dissolved halite.

In contrast, the Cretaceous samples contained more bromide than can be attributed to sea water evaporation. Additional concentration mechanisms were responsible for these higher bromide concentrations.

### Table III. Correlation Coefficients, Tertiary Samples

| | Depth | T.D.S. | Na | Ca | Mg | Cl | Br | I | $HCO_3$ | $SO_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Depth | 1.000 | 0.616 | 0.553 | 0.711 | 0.340 | 0.618 | 0.553 | −0.146 | 0.201 | 0.193 |
| T.D.S. | 0.616 | 1.000 | 0.993 | 0.309 | 0.347 | 0.999 | 0.153 | −0.523 | −0.043 | 0.100 |
| Na | 0.553 | 0.993 | 1.000 | 0.216 | 0.300 | 0.988 | 0.066 | −0.566 | −0.043 | 0.090 |
| Ca | 0.711 | 0.309 | 0.216 | 1.000 | 0.188 | 0.315 | 0.856 | 0.316 | −0.089 | 0.093 |
| Mg | 0.340 | 0.347 | 0.300 | 0.188 | 1.000 | 0.355 | 0.222 | −0.147 | −0.004 | −0.011 |
| Cl | 0.618 | 0.999 | 0.988 | 0.315 | 0.355 | 1.000 | 0.162 | −0.517 | −0.053 | 0.082 |
| Br | 0.553 | 0.153 | 0.066 | 0.856 | 0.222 | 0.162 | 1.000 | 0.413 | −0.217 | 0.001 |
| I | −0.146 | −0.523 | −0.566 | 0.316 | −0.147 | −0.517 | 0.413 | 1.000 | −0.225 | −0.036 |
| $HCO_3$ | 0.210 | −0.043 | −0.043 | −0.089 | −0.004 | −0.053 | −0.217 | −0.225 | 1.000 | 0.207 |
| $SO_4$ | 0.193 | 0.010 | 0.090 | 0.093 | −0.011 | 0.082 | 0.001 | −0.036 | 0.207 | 1.000 |

### Table IV. Correlation Coefficients, Cretaceous Samples

| | Depth | T.D.S. | Na | Ca | Mg | Cl | Br | I | $HCO_3$ | $SO_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Depth | 1.000 | 0.799 | 0.603 | 0.787 | 0.349 | 0.753 | 0.625 | 0.554 | −0.479 | 0.379 |
| T.D.S. | 0.799 | 1.000 | 0.858 | 0.863 | 0.484 | 0.947 | 0.811 | 0.246 | −0.408 | 0.335 |
| Na | 0.603 | 0.858 | 1.000 | 0.506 | 0.287 | 0.797 | 0.588 | 0.214 | −0.209 | 0.296 |
| Ca | 0.787 | 0.863 | 0.506 | 1.000 | 0.446 | 0.819 | 0.788 | 0.238 | −0.459 | 0.281 |
| Mg | 0.349 | 0.484 | 0.287 | 0.446 | 1.000 | 0.489 | 0.533 | −0.030 | −0.320 | 0.014 |
| Cl | 0.753 | 0.947 | 0.797 | 0.819 | 0.489 | 1.000 | 0.755 | 0.226 | −0.404 | 0.315 |
| Br | 0.625 | 0.811 | 0.588 | 0.788 | 0.533 | 0.755 | 1.000 | 0.092 | −0.362 | 0.228 |
| I | 0.554 | 0.246 | 0.214 | 0.238 | −0.030 | 0.226 | 0.092 | 1.000 | −0.077 | 0.268 |
| $HCO_3$ | −0.479 | −0.408 | −0.209 | −0.459 | −0.320 | −0.404 | −0.362 | −0.077 | 1.000 | −0.044 |
| $SO_4$ | 0.379 | 0.335 | 0.296 | 0.281 | 0.014 | 0.315 | 0.228 | 0.268 | −0.044 | 1.000 |

### Table V. Rotated Factor Matrix, All Samples

| Factor | Depth | T.D.S. | Na | Ca | Mg | Cl | Br | I | $HCO_3$ | $SO_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.522 | 0.484 | −0.066 | 0.805 | 0.765 | 0.484 | 0.852 | 0.515 | −0.779 | −0.094 |
| 2 | 0.575 | 0.854 | 0.931 | 0.372 | 0.291 | 0.854 | 0.294 | −0.115 | −0.012 | −0.228 |
| 3 | 0.399 | 0.157 | 0.012 | 0.295 | −0.046 | 0.157 | 0.199 | 0.617 | 0.030 | 0.851 |

### Table VI. Rotated Factor Matrix, Tertiary Samples

| Factor | Depth | T.D.S. | Na | Ca | Mg | Cl | Br | I | $HCO_3$ | $SO_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.682 | 0.907 | 0.687 | 0.856 | 0.690 | 0.876 | 0.870 | −0.004 | −0.565 | 0.131 |
| 2 | 0.577 | 0.358 | 0.370 | 0.262 | −0.184 | 0.345 | 0.111 | 0.873 | 0.015 | 0.655 |

### Table VII. Rotated Factor Matrix, Cretaceous Samples

| Factor | Depth | T.D.S. | Na | Ca | Mg | Cl | Br | I | $HCO_3$ | $SO_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.578 | 0.976 | 0.976 | 0.184 | 0.398 | 0.976 | 0.039 | −0.671 | −0.015 | 0.057 |
| 2 | 0.645 | 0.136 | 0.037 | 0.934 | 0.234 | 0.136 | 0.939 | 0.532 | −0.144 | 0.109 |
| 3 | 0.308 | −0.005 | 0.002 | 0.049 | 0.035 | −0.005 | −0.113 | −0.182 | 0.838 | 0.701 |

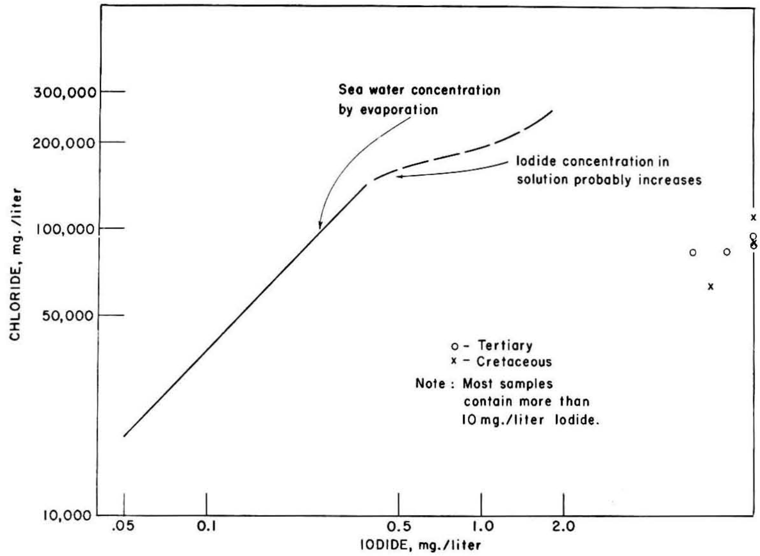

**Figure 2. Iodide *vs.* chloride for some representative Mississippi and Alabama Tertiary and Cretaceous oilfield brines**

*Iodide Concentration*

The distribution of iodide in marine and oceanic silts and interstitial waters indicates that near-shore ocean sediments contain more iodide than deep-sea sediments (Shishkina and Pavlova, 1965). Iodide is selectively captured by flocculated hydroxides. Reduction in low *Eh* environments can cause high accumulations of iodide in interstitial waters (Sugawara, Koyama, *et al.*, 1965).

Iodide has a strong coefficient of fixation in organic matter and, in various states of oxidation, is adsorbed by carbon, clays, and rocks (Kagen and Gel'fer, 1961; De, 1966; Gorgrishvilli, Karkarashvili, *et al.*, 1961; Kojima, 1960).

The adsorption rate increases with temperature and acidity and decreases in the presence of naphthenic acids and mineral salts, especially calcium chloride (Rozen, 1959).

Meteoric water contains iodide enriched relative to chloride 300 to 1000 times compared with sea water (Winchester and Duce, 1965). Seaweeds, such as *Liminaria digitata*, contain 8000 p.p.m. iodide; and corals, such as *Gorgonia Verrucosa*, contain 69,200 p.p.m. iodide (Vinogradov, 1953).

Iodide can be concentrated by several mechanisms. The fact that its adsorption rate decreases in the presence of naphthenic acids and mineral salts is interesting. Several formation waters contain naphthenic acid salts and high concentrations of calcium chloride. These factors may cause desorption or solubilization of iodide in some environments.

Figure 2 illustrates the amount of iodide that can be expected to concentrate in the aqueous phase during sea water evaporite formation. The change in slope represents eutectic factors similar to those used for bromide in Figure 1. Obviously, mechanisms other than evaporite formation cause iodide enrichment in oilfield waters.

*Concentration of Other Ions*

The increased chloride concentration can be attributed to evaporation. Magnesium depletion and calcium enrichment probably result primarily from dolomitization. Bicarbonate depletion is the result of carbonate precipitation. Sulfate depletion is the result of gypsum precipitation and/or bacterial action.

The ionic potentials of elements discussed here are sodium, 0.95; calcium, 0.50; magnesium, 0.33; chlorine, 1.81; bromine, 1.95; and iodine, 2.16. In general, those with the lower potentials are more likely to remain in true ionic solution. However, other factors in addition to evaporite deposition occur. Some of these other factors are diagenesis of sediments including evaporite sediments, metasomatism such as dolomitization, and metamorphism which could cause release of fresher water.

Two distinct phases which can be responsible for the development of connate water from sea water are carbonates and sulfates of calcium and magnesium precipitate as a result of base exchange with clay sediments (DeSitter, 1947), and compact clays form semipermeable membranes to salt ions. As the compaction increases, fresh water is released while the salt ions are restricted (Siever, Garrels, *et al.*, 1961).

### *Rotated Factor Matrix*

The correlation matrices shown in Tables II, III, and IV may be subjected to additional analyses. To understand the underlying relationships of the variables, factor analysis (Kaiser, 1958; McElroy and Kaesler, 1965) can be applied. Factor analysis is used to find the least number of uncorrelated axes representing the hyperspace in which the variables are plotted, to express correlation among the factors by rotating the axes to a simple structure, and to transform the simple structure solution to a primary pattern.

Three factors are shown in Table V, two in Table VI, and three in Table VII. Only these factors are shown, because only they had sizable coefficients.

Interpretation of a factor is made in terms of the squares of its coefficients. Factor 1, Table V, indicates that most of the covariance among properties in the system can be accounted for by the variances of depth, T.D.S., Ca, Mg, Cl, Br, I, and $HCO_3$. There is an identical loading on T.D.S. and Cl, an almost identical loading on Ca and Br, Mg and $HCO_3$, and depth and I. Therefore, principal variance in chemical composition of this system is controlled by the chemical constituents, calcium and bromide. The variances in T.D.S. are closely related to Cl.

Factor 2, Table V, indicates identical loadings on T.D.S. and Cl. The sum of the squares of the coefficients Cl and Br ($0.854^2 + 0.294^2 = 0.815$) approximate that of Na ($0.931^2 = 0.867$). This further corroborates the evidence that variances in T.D.S. are closely related to Cl. The variances in Cl and Br are related to Na, but this portion of the communality is less important than T.D.S. and Cl and Ca and Br.

Factor 3, Table V, shows identical loadings on T.D.S. and Cl and near identical negative loadings for Mg and $HCO_3$. Factors 2 and 3 in Table V indicate that iodide and sulfate vary independently of any other variables.

Factor 1, Table VI, indicates that most of the covariance among the properties in the Tertiary age system can be accounted for by variances of depth, T.D.S., Na, Ca, Mg, Cl, Br, and $HCO_3$. Both factors 1 and 2 show that the principal variance in this hydrochemical system is controlled by Cl and T.D.S., Ca and Br, and Na and Cl. Factor 2 indicates a possible covariance for depth and sulfate.

Factor 1, Table VII, shows that most of the covariance among the properties in the Cretaceous age system can be accounted for by variances in depth, T.D.S., Na, Ca, Mg, and Cl. Identical loadings are shown for T.D.S. and Cl and Na and Cl, in factor 1. Factor 2 indicates identical loadings for T.D.S. and Cl and nearly identical for Ca and Br. Factor 3 shows identical loadings for T.D.S. and Cl. Factors 1 and 2 indicate a possible covariance between depth and I for the Cretaceous age waters.

### *Conclusions*

These waters can be distinguished on the basis of bromide. The principal variance in the chemical composition of the combined Tertiary and Cretaceous waters is controlled by calcium and bromide.

Interesting correlations in the Tertiary waters were found between Cl and T.D.S., Cl and Na, Na and T.D.S., Br and Ca, and Ca and depth. Strong correlations found in the Cretaceous waters were Cl and T.D.S., Ca and Cl, Na and T.D.S., Ca and T.D.S., Br and T.D.S., Na and Cl, Ca and Br, Ca and depth, and Cl and Br.

### *Acknowledgment*

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# Odorous Compounds in Natural Waters. Some Sulfur Compounds Associated with Blue-Green Algae

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■ Several odorous organic sulfur-containing compounds have been identified in cultures of blue-green algae using gas chromatographic techniques. The blue-green algae cultures were bacterially contaminated, and in all but one case the odorous sulfur compounds most probably resulted from bacterial putrefaction of the blue-green algal cells. The organism *Microcystis flos-aquae*, however, was shown to be capable of producing a natural gas odor, which was shown to be isopropyl mercaptan, during periods of active growth. Odorous sulfur compounds produced in decaying blue-green algal cultures and reservoir waters containing blue-green algal blooms included methyl mercaptan, dimethyl sulfide, isobutyl mercaptan, and *n*-butyl mercaptan.

Numerous references associate the presence of malodors and off-tastes in water supplies with the occurrence of high populations of blue-green algae in the source of water supply. These odors, variously described as fishy, aromatic, grassy, and septic (Palmer, 1962), have been reported most often after the peak of the bloom of blue-green algae has passed. Therefore, some of these odorous compounds apparently are the result of cell decay and decomposition.

In the present investigation, both actively growing and actively decaying cultures of various blue-green algae were investigated to determine the nature of the odorous compounds produced. Attention was focused on the sulfur compounds by a combination of factors. First, the blue-green algal cultures under investigation produced odors reminiscent of mercaptans and other organic sulfur compounds. Second, in the study of decaying cultures, one may logically argue that organic sulfur compounds may be present as a result of anaerobic decomposition of cellular material.

Sulfur compounds that are known to be malodorous were associated with two species of marine algae by Challenger and Simpson (1948). Challenger, Bywood, *et al.* (1957) identified dimethyl sulfide in the green alga *Enteromorpha intestinalis* and suggested that the putrid odor associated with decaying algae may be due to a mercaptan. Dimethyl sulfide and methyl mercaptan either together or separately have been found among the volatile constituents of certain green, brown, and red marine algae (Lewin, 1962). Methyl sulfide was in marine algae (Haas, 1935); methyl mercaptan was an aroma constituent of algae (Katayama, 1964) and dimethyl sulfide was in certain seaweeds (Obata, 1951). Collins and Gaines (1964) reported that $H_2S$ was one of the odorous constituents of the actinomycete, *Streptomyces odorifer*.

In previous work on these low molecular weight compounds, separation and identification generally involved the resolution of sulfur compounds into various groups by the use of chemical traps following a distillation step. For example, lead acetate is used to trap $H_2S$, mercuric cyanide to remove mercaptans, and mercuric chloride to trap sulfides. Further chemical tests are then made on the precipitates retained in the traps to permit identification within the various groups of compounds.

In the present work, gas chromatography was used in conjunction with chemical tests and the use of an organoleptic detector or human sensor, to separate and identify several malodorous sulfur compounds associated with cultures of blue-green algae.

## *Materials and Methods*

**Algal Growth System.** The blue-green algae, *Microcystis flos-aquae* and *Oscillatoria chalybia*, studied in this investigation were grown on Medium 11 (Hughes, Gorham, *et al.*, 1958) in 20-liter glass carboys at room temperature (24° to 27° C.) and illuminated by overhead daylight fluorescent bulbs with an intensity of 150 to 200 foot-candles at the culture surface. Air with 0.5% $CO_2$ was used to aerate the cultures continuously. Care was taken to avoid the use of rubber tubing and stoppers in culture vessels (and any other apparatus). All lines were constructed of either glass or Tygon tubing, and corks with Teflon or aluminum foil liners were employed. In early work, both the air supply and the water used in preparation of the culture medium were filtered through granular activated carbon and 0.22-micron membrane filters—precautions that were taken to avoid the introduction of contaminants in the air and water, and that later work showed were unnecessary.

**Organisms and Natural Waters.** *Microcystis flos-aquae* EAWAG 94b was obtained from Alfons Zehnder, EAWAG, Zurich, Switzerland. This culture was unialgal but bacterially contaminated with a gram-negative rod.

*Oscillatoria chalybia* No. 386 was obtained from Robert S. Safferman, Cincinnati Water Laboratory, Federal Water Pollution Control Administration, Cincinnati, Ohio. This culture was unialgal but was bacterially contaminated.

Bloom of *Anabaena spp.* from San Pablo Reservoir, Calif. In April 1966, a 2-liter sample of water from the San Pablo reservoir of the East Bay Municipal Utilities District containing a bloom of a small bead Anabaena was obtained. The water had a putrid odor which intensified greatly after the sample had been stored in the dark at room temperature for three months.

Bloom of Blue-Green Algae from Chabot Reservoir, Oakland, Calif. A sample of reservoir water containing approximately $10^6$ organisms per 100 ml. of *Anabaena spp.* was obtained from the Chabot reservoir of the East Bay Municipal Utilities District. It had a distinct putrid odor.

**Concentration Methods.** Since the odorous compounds in the algal cultures and natural waters studied were present in concentrations too low to be detected by even the most sensitive gas chromatographic detector, a concentration step was necessary prior to gas chromatographic analysis.

Early efforts at concentration involved the use of a series of freeze-out traps (cooled by an acetone–dry ice mixture) on the exit gas from the culture vessels. However, because of the high volatility and ease of oxidation of the compounds under investigation, even three traps in series and rapid sample handling techniques did not prevent significant losses of odorous materials by evaporation and atmospheric oxidation.

The sulfur compounds were concentrated by steam distillation (of the culture fluid containing the algae) at atmospheric pressure in an all-glass apparatus. The distillate was collected in a receiver cooled at 0° C. with an ice-water mixture. Following distillation, the residual liquid in the distillation flask was generally devoid of odor.

**Analytical Methods.** Gas chromatography was used as the primary separation and identification tool. The three types of detector employed were the hydrogen flame ionization detector, the microcoulometric detector, and the human sensor or organoleptic detector.

The majority of the analyses were carried out using hydrogen flame and human sensor detectors on a Varian Aerograph Model 1520-B dual column, matrix temperature programmed gas chromatograph. Helium was used as a carrier gas and ultrapure tank $H_2$ and tank air were used as sources of fuel for the hydrogen flame detector. Great effort was taken to ensure the stability of He, $H_2$, and air flows because detectability in the low parts-per-billion range was required even after a concentration step. The gas lines were fitted with Model 67-1 Fisher Governor regulators, 4.6-liter surge tanks made from government surplus breathing oxygen tanks, Whitey OVS2 needle valves, and 7-micron Nupro F Series Inline filters. The instrument was equipped with an Aerograph No. 57-045 multicolumn valve. A variety of standard stainless steel analytical columns $^1/_8$ inch (2.4-mm. I.D.) were used, with both polar and nonpolar liquid phases and an uncoated Poropak column (Table I). While glass columns and glass injector inserts have been recommended frequently for the gas chromatographic analysis of sulfur compounds, particularly at high operating temperatures, the use of stainless steel columns was satisfactory throughout this study. Several standard organic mercaptans and sulfides were resolved gas chromatographically using stainless steel columns at operating temperatures of up to 140° C. without any indication of loss through chemical reaction.

Besides the routine use of the hydrogen flame detector, each resolved peak was smelled at the detector (on a repeated analysis with the flame extinguished) using the human sensor technique. This technique is used extensively in the perfume industry (Fuller, 1964) and together with retention times on various chromatographic columns provides a powerful aid to identification. For example, while ethyl mercaptan and dimethyl sulfide have almost the same retention time on many gas chromatographic columns, on the basis of odor there is little doubt as to which compound is present, since ethyl mercaptan has a natural gas type of smell while dimethyl sulfide has a distinctly putrid odor.

All compounds identified or tentatively identified in this paper have been analyzed by comparison with known standards of the resolved compound using the human sensor as well as the hydrogen flame detector; and in the opinion of the person(s) smelling the column effluents, the odor of the identified unknowns and that of the suggested standard compound are indistinguishable.

The sample analyzed by one or other of these chromatographic techniques consisted of a few milliliters (usually 2.5 ml.) of the head space gas drawn from a warmed flask of distillate or other concentrate by puncturing an aluminum foil cap with a syringe.

**Chemical Spot Tests.** Spot tests were employed both alone and in conjunction with gas chromatography as aids to the identification of sulfur compounds.

Mercaptans were tested for by the method of Feigl (1966) using $CuCl_2$ and hydroxylamine. A positive reaction was indicated by the appearance of a yellow or brown precipitate.

Testing for hydrogen sulfide was performed by acidifying a portion of steam distillate in a small Erlenmeyer flask with HCl, then warming the acidified solution slowly to boiling with a piece of moist lead acetate paper held over the mouth of the flask. A brown or black discoloration indicated a positive reaction.

No sensitive or reasonably specific spot test for low concentrations of sulfides or disulfides was found.

Spot testing was used in conjunction with gas chromatography in a fashion similar to that described by Hoff and Feit (1964). For example, the spot test for mercaptans (Feigl, 1966) was used on a 10 to 20 times larger scale. Head space gas from before and after treatment with the spot test reagents was analyzed gas chromatographically under the same chromatographic conditions. Because of the reactions

$$2\ RS^- + 2\ Cu^{+2} \rightarrow Cu_2^{+2} + RSSR$$

$$Cu_2^{+2} + 2\ RS^- \rightarrow Cu_2\ (RS)_2$$

the mercaptan peak in the original trace was eliminated (Figure 1). This procedure is applicable to samples in which the concentration of reactant is too low to give a visible, positive spot plate reaction so long as even a small chromatographic peak can be obtained.

## *Results*

None of the cultures of actively growing or decaying blue-green algae or samples of reservoir water containing blue-green algae contained concentrations of $H_2S$ detectable by spot testing or by the microcoulometric detector.

*Microcystis flos-aquae*. This organism when growing actively possessed a distinct "natural gas" odor of some pungency. Although maximum growth on Medium 11 under the conditions described took from 2 to 3 weeks, this organism

**Table I. Retention Times of Sulfur Compounds on Various Gas Chromatographic Columns**

| Column and Operating Conditions | Column 1, 2-Meter, 15% FFAP on 60- to 80-Mesh Chromosorb W, Reg. | | | Column 2 1.5-Meter, 15% Carbowax 20 M on 60- to 80-Mesh Chromosorb W, Reg. | Column 3 50-Cm., Porapak Q 100- to 120-Mesh Uncoated | | Column 4 3-Meter, 20% DC-710 on 60- to 80-Mesh Chromosorb W AW with MCT Detector | Column 5 3-Meter, 1% SF96 (50) + 0.05% Igepal on 100- to 120-Mesh Chromosorb G, HMDS | Column 6 1.5-Meter, 20% Carbowax 1540 on 60- to 80-Mesh Chromosorb W, Reg. |
|---|---|---|---|---|---|---|---|---|---|
| | a | b | c | a | a | b | a | a | a |
| Helium flow rate, ml./min. | 35 | 20 | 35 | 20 | 75 | 60 | . . . | 45 | 65 |
| Column temperature, ° C. | 75 | 32 | 40 | 36 | 124 | 100 | . . . | 32 | 75 |
| Retention time, seconds | | | | | | | | | |
| Methyl mercaptan, $CH_3 \cdot SH$ | . . . | . . . | 63 | 42 | . . . | 27 | 120 | . . . | 11 |
| Ethyl mercaptan, $CH_3 \cdot CH_2 \cdot SH$ | . . . | . . . | 83 | 61 | . . . | 68 | 210 | . . . | 17 |
| Propyl mercaptan, $CH_3 \cdot CH_2 \cdot CH_2 \cdot SH$ | . . . | . . . | . . . | . . . | . . . | . . . | 390 | . . . | . . . |
| Isopropyl mercaptan, $(CH_3)_2 \cdot CH \cdot SH$ | . . . | 117 | . . . | 72 | 97 | . . . | 240 | 285 | . . . |
| Butyl mercaptan, $CH_3 \cdot CH_2 \cdot CH_2CH_2 \cdot SH$ | . . . | . . . | . . . | . . . | . . . | . . . | 750 | . . . | . . . |
| Isobutyl mercaptan, $(CH_3)_2 \cdot CH \cdot CH_2 \cdot SH$ | . . . | . . . | . . . | . . . | . . . | . . . | 630 | . . . | . . . |
| Dimethyl sulfide, $CH_3 \cdot S \cdot CH_3$ | 50 | . . . | 88 | 54 | . . . | 72 | 240 | 180 | 120 |
| Dimethyl disulfide, $CH_3 \cdot SS \cdot CH_3$ | . . . | . . . | . . . | . . . | . . . | . . . | 1080 | 505 | . . . |

Columns 1, 2, 3, 5, 6: $H_2$ flow 15 ml./min.
Air flow 315 ml./min.
Injector and detector 140° C. ± 10° C.
Column 4: Temperature programmed 45–200° C. at 2° C./min.
$N_2$ carrier gas flow 15 ml./min.

began to produce the pungent natural gas odor a few days following inoculation of the culture.

Gas chromatographic analysis of the steam distillates of the *Microcystis flos-aquae* culture showed the presence of a single odorous compound which was identified by comparison of retention times and odor of the resolved peak with standards on five columns (Table II) as isopropyl mercaptan. The peak was eliminated by spot testing with the Feigl (1966) reagent for mercaptans (Figure 1). In addition, the compound produced a response from the microcoulometric detector and on this instrument had a retention time identical with standard isopropyl mercaptan.

The natural gas odor was shown not to be produced by the bacterial contaminant by the following experiment. The *Microcystis flos-aquae* culture was sonicated and the resulting sonicate plated out on nutrient agar. The bacterial colonies that developed were then transferred to Medium 11 (Hughes, Gorham, *et al.*, 1958) to which an extract of *Microcystis flos-*

**Table II. Retention Time Data for Odorous Peaks from Various Blue-Green Algal Cultures and Reservoir Waters**

| Retention Time, Sec. of Odorous Peaks from Indicated Sample Materials | Column 1 | | | Column 2 | Column 3 | | Column 4 | Column 5 | Column 6 | Indicated Compound |
|---|---|---|---|---|---|---|---|---|---|---|
| | a | b | c | a | a | b | a | a | a | |
| *Microcystis flos-aquae,* actively growing | ... | 114 | ... | 70 | 98 | ... | ... | ... | ... | Isopropyl mercaptan |
| *Microcystis flos-aquae,* | ... | ... | ... | ... | ... | ... | 240 | 285 | ... | Isopropyl mercaptan |
| 2-month-old culture | ... | ... | ... | ... | ... | ... | 613 | ... | ... | Isobutyl mercaptan |
| | ... | ... | ... | ... | ... | ... | 785 | ... | ... | *n*-Butyl mercaptan |
| | ... | ... | ... | ... | ... | ... | 1042 | 500 | ... | Dimethyl disulfide |
| *Oscillatoria chalybia* | ... | ... | 65 | 42 | ... | 28 | ... | ... | ... | Methyl mercaptan |
| 2-month-old-culture | ... | ... | 92 | 56 | ... | 71 | ... | ... | ... | Dimethyl sulfide |
| *Oscillatoria chalybia* | ... | ... | ... | ... | ... | ... | 132 | ... | ... | Methyl mercaptan |
| 6-month-old culture | ... | ... | ... | ... | ... | ... | 612 | ... | ... | Isobutyl mercaptan |
| | ... | ... | ... | ... | ... | ... | 780 | ... | ... | *n*-Butyl mercaptan |
| | ... | ... | ... | ... | ... | ... | 1068 | 500 | ... | Dimethyl disulfide |
| *Anabaena spp.* bloom San Pablo reservoir | ... | ... | 90 | ... | ... | ... | ... | 180 | 104 | Dimethyl sulfide |
| *Anabaena spp.* bloom Chabot reservoir | 49 | ... | ... | ... | ... | ... | ... | ... | ... | Dimethyl sulfide |

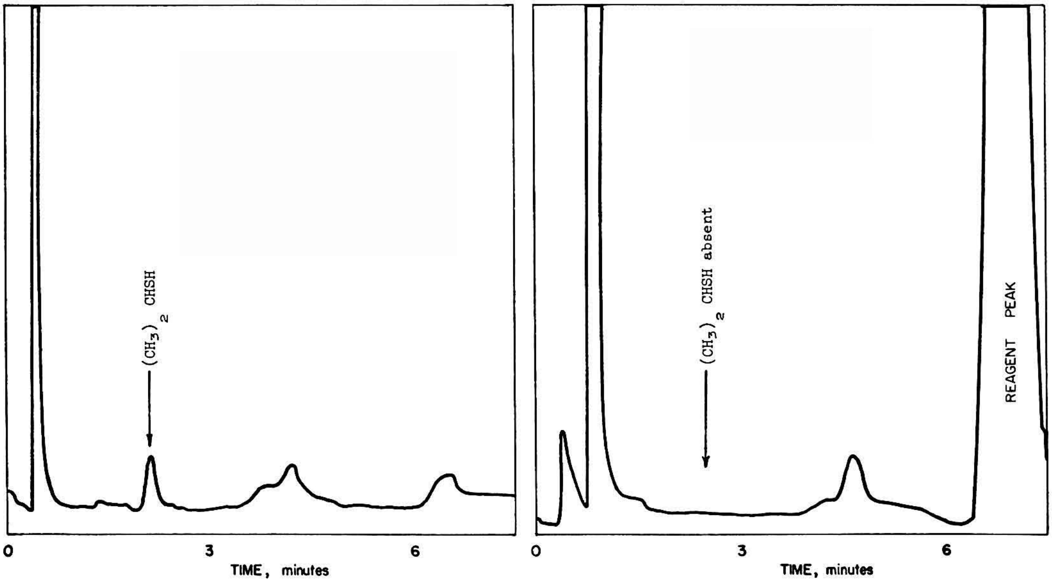

Figure 1. Use of specific spot tests in combination with gas chromatography

**Left, steam distillate from *Microcystis flos-aquae* culture fluid. Column: 3 mm. × 2 meters, 15% FFAP on 60- to 80-mesh Chromosorb W. Temperature: detector, 145° C.; injector, 130° C.; column, 32° C. Carrier gas: helium, 25 ml./min.**
**Detector: flame 1**
**Right, steam distillate from *Microcystis flos-aquae* culture fluid after treatment with $CuCl_2$-$NH_2OH$ reagent, specific for mercaptans**

*aquae*, prepared by the method of De (1939), had been added. After a period of 72 hours' growth at 37° C. on this medium, no natural gas odor was detectable, as it certainly would have been if live *Microcystis flos-aquae* had been present. Rather, the Medium 11 plus algal extract possessed a slightly putrid odor, typical of the putrid taint encountered in old *Microcystis flos-aquae* cultures.

*Microcystis flos-aquae* cultures were allowed to grow for approximately 2 months, under continuous aeration, and in these older cultures the original natural gas odor became modified with a putrid taint. Gas chromatographic analysis of the head space gas from steam distillates of these old cultures revealed, in addition to the major isopropyl mercaptan peak, several other odorous peaks. Use of two columns, the microcoulometric detector, and the human sensor permitted the positive identification of dimethyl disulfide as one of the constituents of the putrid taint in the odor. Two other odorous components were tentatively identified as isobutyl mercaptan and *n*-butyl mercaptan on the basis of data from one column and the microcoulometric system (Table II).

*Oscillatoria chalybia.* Actively growing laboratory cultures of *O. chalybia* on Medium 11 had no malodor; the only smell associated with such actively growing cultures was a very slight grassy aroma. However, when the cultures had been grown under aeration for about 2 months and a significant discoloration (yellowing) of the alga had taken place, the culture gas took on a distinct putrid odor. Gas chromatographic analysis of the steam distillate of the culture showed the presence of two odorous peaks which were positively identified as dimethyl sulfide and methyl mercaptan. At this time, methyl mercaptan was present in a greater amount than dimethyl sulfide.

A 2-month-old *O. chalybia* culture was allowed to stand quiescently (without aeration) in the light at room temperature for 4 months longer. At the end of this period, the culture had developed a particularly revolting putrid odor. Gas chromatographic analysis confirmed the presence of methyl mercaptan and dimethyl disulfide. No dimethyl sulfide was detected. In addition, as with the old culture of *Microcystis flos-aquae*, *n*-butyl mercaptan and isobutyl mercaptan were tentatively identified. The quantity of methyl mercaptan was small in comparison with the amounts of the other odorous components.

**Reservoir Waters from the San Francisco Bay Area.** Reservoir water from EBMUD San Pablo reservoir containing a bloom of a small bead *Anabaena spp.* was stored quiescently in the laboratory for 3 months, after which time the putrid odor that it originally possessed had intensified considerably. While only a single gas chromatographic column was used for the analysis of the steam distillate of this material, on the basis of these data and the unmistakable similarity of the odor of the resolved compound, this odorous material is identified as dimethyl sulfide.

A water sample from the EBMUD Chabot reservoir following an algal bloom of *Anabaena spp.* also possessed a putrid odor. Gas chromatographic analysis of the steam distillates of this water using three columns with hydrogen flame and human sensor detectors confirmed the presence of dimethyl sulfide as the only odorous component.

## *Conclusions*

As a result of these findings, the authors feel that these sulfur compounds and others of a similar nature may be important in the production of taste and odor in stored surface water supplies, especially following the peak and resulting bacterial decay of an algal bloom. The rapid rate of atmospheric oxidation and the high volatility of these compounds, however, will probably prevent their becoming a serious taste and odor problem, since they should be easily removed by aeration.

The odor of dimethyl sulfide at low concentrations strongly resembles the fishy odor commonly associated with amines such as methylamine and ethylamine. The fishy odors often reported as being associated with certain blue-green algal blooms may therefore be caused by the presence of dimethyl sulfide and not, as commonly postulated, by the presence of an amine.

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# Nitrate and Other Water Pollutants under Fields and Feedlots

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■ Agriculture's effect on nitrate pollution of ground water was investigated in the South Platte valley of Colorado. The valley is intensively farmed and contains many concentrated livestock feeding operations. A water table, generally between 3 and 20 meters below the surface, underlies much of the area. The average total nitrate-nitrogen to a depth of 6.7 meters in the profiles for the various kinds of land use was: alfalfa (*Medicago sativa*) (13 cores), 70; native grassland (17 cores), 81; cultivated dryland (21 cores), 233; irrigated fields not in alfalfa (28 cores), 452; and feedlots (47 cores), 1282 kg. per hectare. Ground water samples often contained high concentrations of nitrate, and those obtained beneath feedlots contained ammonium-nitrogen and organic carbon.

Possible agricultural sources of ground water pollutants include fertilizer materials applied to soil and wastes from concentrated livestock feeding operations. Their contribution to pollution of underground water was studied in the middle South Platte River valley in Colorado. This valley is an intensely farmed irrigated area underlain with a water table varying from about 3 to 20 meters beneath the surface. Most of the 621,000 cattle in feedlots in Colorado (as of Feb. 1, 1967) are located in this valley. Nonirrigated pasture and cropland surrounds the valley and is part of the semiarid High Plains.

## *Experimental*

One-hundred twenty-nine cores extending from the surface to the water table or bedrock from sites of differing land use in this area were obtained and analyzed. The cores were obtained during the period of April 26 through July 21, 1966. Locations were chosen to represent varying soils, water table depths, and soil uses. Insofar as possible, locations were selected that had feedlots, irrigated fields, and nonirrigated fields within the same soil type. This selection allows a comparison of the effects of feedlot operations with effects of intensified farming where heavy applications of plant nutrients are frequent. Use of commercial fertilizers in the area have been steadily increasing, although there is no evidence of their general excessive use. The highest rate of fertilizer nitrogen applied on any of the fields sampled was about 175 kg. per ha. The nonirrigated areas served as a control, since these fields have never received any fertilizers.

Emphasis was placed on the quantity of nitrate in transit to the water table, but other pollutants were also measured. Nitrate is of concern because of the potential health hazard to livestock and humans (particularly infants) that high amounts of nitrate in water present. A detailed report, including descriptions of equipment used to obtain unwetted, undisturbed cores and of analytical procedures, is being published elsewhere (Stewart, Viets, *et al.*, in press). The detailed report also includes estimates of fertilizer usage, feedlot ages, and the texture and water content at all depths for all of the cores.

## *Results and Discussion*

**Nitrate in Core Samples.** Nitrate found at various depths in cores from different land uses is presented in Figure 1. Bar heights show the number of cores at the specified depth that contained nitrate (expressed as p.p.m. of N in soil on dry-weight basis) in the quantity indicated by the bar position. Nitrate was determined on either 15- or 30-cm. depth increments of the entire core, but only data from intermittent depths are presented here. As distance from the soil surface increases, fewer cores are represented, because the majority of the cores were less than 12 meters long and several were less than 5 meters.

Data for cores from nonirrigated areas are separated into those from cultivated areas and those from areas in native sod. Nonirrigated cultivated fields from which cores were taken are usually cropped only every second year in a fallow-crop system and, with one exception, had never been fertilized. Average annual precipitation in the area is 40 cm. A difference in the nitrate distribution patterns of the two groups is apparent. Most cores from sod areas were nearly free from nitrate. For example, at the 3.3- to 3.6-meter interval, 10 of the 16 cores contained no nitrate (less than 0.5 p.p.m. of nitrate-N). At the same depth in cores from cultivated areas, only five of 24 samples were free of nitrate; four samples contained more than 3 p.p.m. of nitrate-N. Differences between the nitrate contents of cores from cultivated areas and those from sod areas were largest at depths greater than 2 meters below the soil surface, which is below the rooting depth of most crops grown under dryland conditions. This accumulation of nitrate under cultivated dryland sites (this can also be seen in Figure 2, which is presented later in the text) is significant in relation to the historic loss of total nitrogen during cultivation. Several studies have shown that total nitrogen in these soils decreases about 50% during 30 to 50 years of cultivation. A large portion of this decrease cannot be accounted for by crop removal. Leaching losses have generally been considered negligible in the Great Plains because of the low rainfall, and losses by volatilization and erosion have been emphasized. Findings of this study suggest that leaching losses may have been greatly underestimated, even though the rainfall in the study area averages only about 40 cm. a year. Nitrogenous compounds under sod areas are not subject to the same degree of leaching because grass is always present to absorb nitrate as it is released from decomposition of organic matter and dead plants. Hydraulic conductivity measurements indicated that the average rate of downward movement of water was essentially the same beneath the sod and cultivated areas, about 2.5 cm. per year (cubic centimeters of water per square centimeter of soil).

Cores from irrigated fields are divided into two groups—those from fields in alfalfa (*Medicago sativa*) and those from fields planted to other crops, primarily sugar beets (*Beta vulgaris*) and corn (*Zea mays*). There is a striking difference in the amounts of nitrate present in these two groups. Cores obtained from alfalfa fields contained little nitrate. For example, at the 2.4- to 2.7-meter depth, 11 of the 13 cores were free from nitrate. Similar results were obtained at the other depths. In contrast, cores from irrigated fields in other crops contained significant quantities of nitrate. At the 2.4- to 2.7-meter interval for these cores, only nine of the 25 cores were free of nitrate, and five cores contained more than 3 p.p.m. of N as nitrate. At the 7.2- to 7.5-meter depth, one core contained no nitrate-N, seven cores showed concentrations between 1 and 3 p.p.m., and one core contained more than 3 p.p.m. of nitrate-N. When expressed as concentration in the soil solution, the nitrate-N concentrations were generally between 20 and 40 p.p.m. Hydraulic conductivity measurements indicated an average downward movement of 8.9 cm. of water annually under the irrigated fields growing crops other than alfalfa. On the basis of these measurements, an average of approximately 25 kg. of nitrate-nitrogen per hectare is lost annually from these fields to the water table.

The hydraulic conductivity value reported is for the profile at its water content at sampling and may not be completely valid on a year-round basis. In the previous irrigation season, rates might have been higher than those measured in samples taken in the spring of 1966 after the profile had a chance to drain much of the irrigation water accumulated during the previous season. Reported values, therefore, probably represent the minimum. Nitrate concentrations under al-

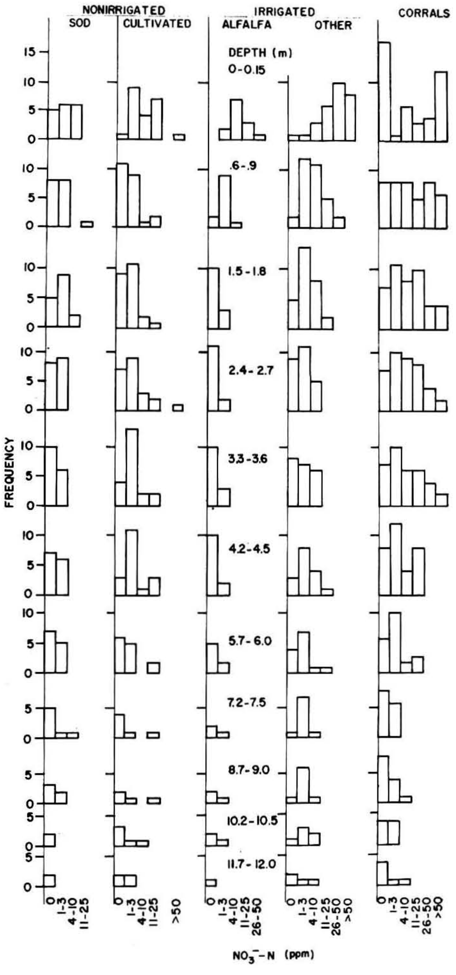

**Figure 1. Histograms showing the distribution of nitrate-N at increasing depths for cores from different land use areas**

**Table I. Chemical Data for Water Samples from Surface of Ground Water Reservoir beneath Four Feedlots and Adjacent Irrigated Fields**

| | Core No. | Depth to Water Table, M. | $NO_3$-N, P.P.M. | $NH_4$-N, P.P.M. | Organic C, P.P.M. | P, P.P.M. | Redox Potential, Mv. |
|---|---|---|---|---|---|---|---|
| Feedlot | 7-E | 10 | 8.6 | 5.1 | 130 | 0.25 | −340 |
| Irrigated field | 7-B | 10 | 0.1 | 0.0 | 18 | 0.06 | 300 |
| Feedlot | 9-F | 5 | 18 | 5.7 | 130 | 0.36 | −310 |
| Irrigated field | 9-C | 3 | 31 | 0.1 | 12 | 0.04 | 360 |
| Feedlot | 9-E | 4 | 21 | 5.8 | 90 | 0.22 | 340 |
| Irrigated field | 9-J | 3 | 8.5 | 0.0 | 9 | 0.01 | 430 |
| Feedlot | 16-B | 11 | 1.1 | 38 | 170 | 1.3 | 100 |
| Irrigated field | 16-D | 11 | 18 | 0.4 | 26 | 0.05 | 430 |

falfa fields are low because no nitrogen fertilizers are applied to this crop and because alfalfa is a very deep-rooted plant which can remove nitrate from greater depths of the profile. The average downward movement of water under alfalfa fields was 9.6 cm. per year.

Amounts of nitrate found under feedlots were extremely variable. The totals found ranged from nearly none to more than 4500 kg. of nitrate-nitrogen per hectare in a 7-meter profile. If this much nitrate were leached from a 1-hectare feedlot, the nitrate-N level of 450,000 cubic meters of water could be raised to the 10-p.p.m. level considered as the maximum safe limit by the U. S. Public Health Service. This amount of water would approximately equal the free water under 20 hectares for much of the area covered by this study. Hydraulic conductivity measurements on core samples from beneath feedlots indicated that the average downward movement was 5.6 cm. per year.

Samples from the shallow depths of the corral cores generally contained either high levels of nitrate or none. This is illustrated by the *U* shape of the histogram for the 0- to 0.15-meter depth (Figure 1). Nitrate was not found in samples with redox potentials less than 300 mv., indicating that nitrate was either not formed, or was reduced under feedlots that had profiles lacking oxygen. The low oxygen level in these profiles probably resulted from a high biological oxygen demand induced by the presence of large amounts of organic carbon. Redox potential measurements made on the first meter of several of the cores from corrals were very low and appeared to depend on feedlot management, feedlot age, and the water content of the profile. There were some indications that denitrification was also occurring under some feedlots at depths greater than 6 or 7 meters. The redox potentials at these depths were not exceedingly low, but bacterial counts were much higher under corrals, particularly at the lower depths, than they were under cultivated fields. There also appeared to be a good relation between the magnitude of the microbial population and the occurrence of nitrite. This observation, together with data showing the absence of nitrifying bacteria in the soil layers containing

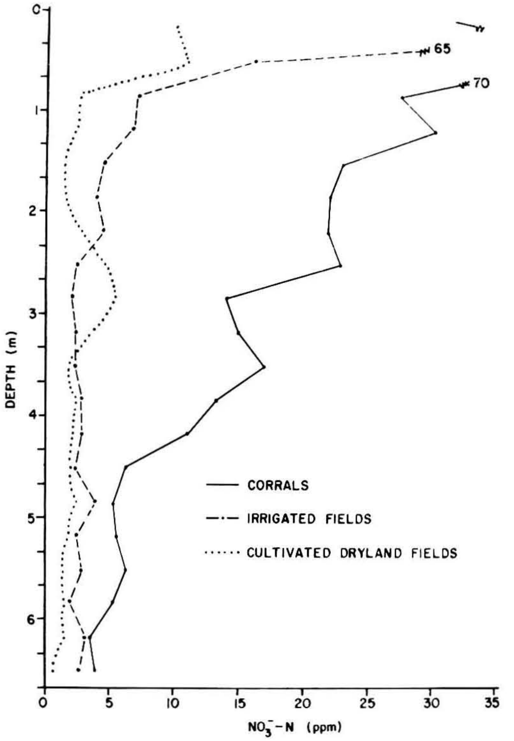

**Figure 2. Average nitrate-N distribution with depth of profiles**

nitrite, justifies the assumption that enzymatic denitrification was occurring in those portions of the profile containing increased numbers of soil microorganisms. Consequently, much of the nitrate found under feedlots will probably never reach the water table.

Feedlots, ranging in ages from about 5 to 90 years, were sampled. There were, however, no clear-cut trends regarding the effect of feedlot age on nitrate present beneath the feedlot. The differences in stocking rates and feedlot management were so varied that the effect of age could not be adequately assessed.

Figure 2 shows the average nitrate distribution with depth of profiles from feedlots (47 cores), irrigated fields in crops excluding alfalfa (28 cores), and dryland cropped fields (21 cores). The comparatively high nitrate concentrations under corrals and the decrease with depth, presumably due to denitrification, is apparent. The accumulation of nitrate between 2.5 and 3.5 meters below the rooting depth of dryland crops is significant in relation to the historic loss of total nitrogen from the surface of dryland cropped soils. The nitrate concentrations under native grassland (17 cores) and alfalfa (13 cores) at the various depths were very low and are not shown. The average total nitrate-nitrogen to a depth of 6.7 meters in the profiles for the various kinds of land use was: alfalfa, 70; native grassland, 81; cultivated dryland, 233; irrigated fields not in alfalfa, 452; and feedlots, 1282 kg. per hectare.

**Analyses of Water Samples.** Water samples were obtained from the core holes at many of the locations. The largest differences between waters collected under corrals and irrigated fields were in their concentrations of ammonium and organic carbon. The average concentration of ammonium-N of the waters from beneath 28 irrigated fields was 0.2 p.p.m., and only two samples contained as much as 1 p.p.m. On the other hand, waters from beneath 29 feedlots averaged 4.5 p.p.m. of N as ammonium. Fifteen of these contained more than 1 p.p.m., seven of which were above 5 p.p.m. The highest concentration of ammonium-N was 38 p.p.m. Similar differences were found in the organic carbon concentrations. Organic carbon in water samples from irrigated fields averaged 14 p.p.m., and the highest value was 29 p.p.m. Waters from beneath feedlots averaged 73 p.p.m. of organic C; 14 of the 20 samples contained more than 30 p.p.m.; and 6 of the 14 exceeded 100 p.p.m. The highest concentration of organic carbon found in a water sample was 300 p.p.m. Generally, water samples high in organic C contained high amounts of ammonium-N. Total soluble phosphorus was also usually higher under corrals. Some of the more striking data obtained from chemical analysis of water samples from beneath four corrals and adjacent irrigated fields are shown in Table I. The differences in concentrations of pollutants in other pairs of samples were not always as large as those shown but showed the same trends. The water samples were obtained from the surface of the ground water reservoir and, therefore, are not necessarily representative of the water in a domestic well at the same site. However, the results do give some indication of the kinds and amounts of materials moving through the soil to the ground water.

## *Conclusion*

Data presented show that nitrate is moving through the soil and into the ground water supply under both feedlots and irrigated fields in crops, excluding alfalfa. Although much larger amounts of nitrate are present under feedlots per unit area, indications are that irrigated lands are contributing more total nitrate to the ground water. The ratio of irrigated land to that in feedlots for the study area is approximately 200 to 1. Feedlots, however, are usually located near the homestead and may have a pronounced effect on the water quality from domestic wells. The findings that water under feedlots frequently contained ammonium (or a compound releasing ammonium) and organic carbon, and had a very offensive odor cause further concern about the effect of feedlots on underground water supplies.

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# Atrazine Losses from Fallow Land Caused by Runoff and Erosion

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■ Measurements were made of atrazine contained in washoff from fallow plots of Cecil soil (6.5% slope). The herbicide was surface applied at 3 pounds per acre and simulated rainfall was used to produce runoff and erosion. The results indicate that atrazine is transported in small but significant amounts in washoff from field plots. A 10-year frequency storm (2.5 inches in 1 hour), occurring 96 hours after herbicide application, caused atrazine losses of 7.3%. Losses resulting from a common size storm (0.5 inch) were 75% less or 0.06 pound per acre. Greater losses resulted when rain was applied immediately after herbicide application. Losses of 0.1 pound per acre and less would be most frequently encountered under actual field conditions. Atrazine content in washoff was highest during early stages of runoff. Concentrations in the soil fraction of the washoff were higher than in the water fraction. However, most of the atrazine transported was associated with the water fraction because of the greater amounts of water lost as compared with soil.

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Water quality and sources of water contamination have become subjects of increasing concern to conservationists and others in recent years. Pesticides carried by runoff and erosion from agricultural lands have often been indicated as a prime source of pollution.

There is evidence that pollution from pesticides can occur. Some pesticides have been identified in rivers and streams in various parts of the country (Cottam, 1961; Nicholson, 1965). The amounts reported have usually been very small; however, little factual information is available on quantitative losses of pesticides in washoff from agricultural lands. In the only reported study of its kind to date, Barnett, Hauser, *et al.* (1967), working on fallow plots of Cecil soil (5% slope), showed that losses in washoff of the butylether ester and amine salt forms of 2,4-D applied at a rate of 2.2 pounds per acre were 13 and 4%, respectively, following a 30-minute rain of 1.25 inches.

Atrazine is one of the herbicides used most often in the Southeast. It is usually surface applied to cultivated soils. This mode of application and the bare soil condition suggests that intense rains following the herbicide application could result in significant losses of atrazine in the washoff. However, at the present time there are little or no factual data available on movement of atrazine in washoff.

This paper reports the results of a study on the rate and magnitude of atrazine losses caused by runoff and erosion from cultivated agricultural soils.

## *Experimental Procedure*

This investigation was conducted at Watkinsville, Ga., in 1965 on a Cecil sandy loam soil of 6.5% slope. This soil is representative of 22 million acres of agricultural land in the Southern Piedmont land resource area. Soil from the site used in this study had 1.05% organic carbon, a pH of 5.5, and an exchange capacity of 3.2 meq. per 100 grams of soil.

The field area used in the study was plowed to a 6-inch depth and harrowed one week before the experiment was run. Immediately before herbicide application, plot surfaces were smoothed by hand and then harrowed parallel to the slope with a drag harrow. This method of preparation provided plot surfaces of uniform slopes and erodibilities.

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) was applied at a rate of 3 pounds per acre to 6 × 35 foot plots, 1 and 96 hours before test storms. An 80% wettable powder formulation of atrazine was sprinkled over the plot surface. Treatments and control plots were replicated twice.

A rainfall simulator (Meyer and McCune, 1958) was used to provide erosional energy. Water distribution was achieved through a series of overhead nozzles directed downward and operating at 6 p.s.i. A rainfall intensity of 2.5 inches per hour with a storm duration of 1 hour was used. Soil and water losses were measured and sampled at the lower edge of the plot.

Washoff samples for atrazine determinations were taken from each plot during the first minute after runoff began and every 5 minutes thereafter until runoff stopped. Samples were collected in 1-quart bottles, sealed with a stopper covered with aluminum foil, and then stored in a refrigerator at 35–40° F. until chemical determinations were made.

Soil samples were taken from plots 24 hours after the test storm for determinations of atrazine content. Soil cores were taken from three locations per plot to a depth of 48 inches and were divided into 6-inch increments except for the top 6-inch portion which was further divided into 3-inch sections. Samples from each depth were composited, transported to the processing area, and air-dried on plastic sheets for 96 hours. The samples were then pulverized, placed in metal cans, and refrigerated at 35–40° F. until time for chemical determination.

Atrazine determinations were adjusted on the basis of recovery studies conducted on samples from an untreated plot in each replication. Washoff and soil samples from these two untreated plots were fortified in the field with known amounts of atrazine at the same time samples from treated plots were collected. These samples were carried through storage and analysis along with samples from treated plots. Recoveries from these fortified washoff and soil samples were 95 and 75%, respectively.

The analytical method used was a modification of the one reported by Knüsli, Burchfield, *et al.* (1964). Chloroform was used for extracting atrazine from both the soil and the washoff samples. Soil samples (50 grams) were extracted with 100 ml. of chloroform on a Soxhlet apparatus for 4 hours. After being evaporated to approximately 10 ml. with a gentle air stream, the extract was cleaned up by transferring the extract with washings to a chromatographic column containing 5 grams of Woelm basic aluminum oxide, activity grade IV (9 to 1, basic alumina-water). Fifty milliliters of chloroform-ether (95 to 5) were added to elute the atrazine from the column. The collected sample was evaporated to approximately 20 ml. and then transferred with washings to a 250-ml. separatory funnel. Two milliliters of 50% $H_2SO_4$ were added, and the sample was shaken every 15 minutes for 2 hours. Twenty milliliters of water were added and mixed by shaking for 15 minutes. After the layers separated for 2 hours, the chloroform layer was drained and discarded. The aqueous layer was collected in a glass-stoppered flask. An aliquot of the aqueous layer was transferred to a 1-cm. quartz cell and read on a Beckman DU spectrophotometer at 227, 241, and 257 mμ, utilizing the base line technique (Knüsli, Burchfield, *et al.*, 1964) for background correction. Reagent blanks and samples from untreated field plots were used in making background corrections. Standard curves were prepared using known amounts of atrazine.

Washoff samples were brought to room temperature and approximately 5 grams of $MgCO_3$–$Ca(OH)_2$ (10 to 4) were added as a flocculating agent. Samples were shaken and then vacuum filtered through Whatman No. 42 filter paper using a Büchner funnel. The soil fraction was air-dried, extracted, and analyzed as above. Appropriate size aliquots of the water fraction (100 to 500 ml. depending on sample concentration) were extracted three times with chloroform (100-, 75-, and 50-ml. portions for 100-ml. aliquots and 150, 100, and 100 ml. for 500-ml. aliquots). Analysis on the combined extract was completed by the same procedure used for soils. The detection limit of the method for 50-gram soil samples and 500-ml. water samples was 0.2 and 0.02 p.p.m., respectively.

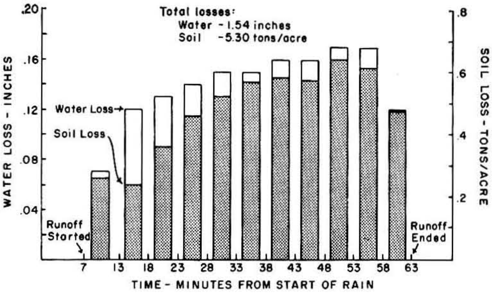

**Figure 1. Soil and water losses by time periods resulting from a 1-hour rain of 2.5 inches (fallow Cecil soil, 6.5% slope)**

*Results and Discussion*

Soil and water losses resulting from a 1-hour test storm of 2.5 inches of simulated rainfall are shown by periods in Figure 1. Runoff and soil loss began 7 minutes after the test storm started. The quantity of water lost in the first minute was very low and was added to that from the next 5-minute increment to give a 6-minute increment for the 7- to 13-minute period. Runoff continued 3 minutes after the storm ended. Water and soil loss rates were lowest during the early stages of runoff and increased to a maximum just before the rain ended.

Atrazine quantities (pounds per acre) removed in the washoff material (water and soil fractions) are shown in Figure 2 for the same time intervals as in Figure 1. Losses were highest during the early stages when runoff rates were lowest. During the latter storm stages when runoff rates were highest, atrazine amounts lost in the washoff were relatively small. Atrazine concentrations (parts per million) in the washoff material showed a similar trend with duration of runoff (Table I). Differences between time periods for both concentrations and amounts lost were significant at the 0.01 probability level.

Throughout the entire runoff period, both concentrations and amounts lost were about 50% lower where atrazine was applied 96 hours before the start of rain than where applied 1 hour before the rain (Table I and Figure 2). These differences were highly significant. Atrazine concentrations in the washoff material for the 1-hour treatment ranged from 10.34 p.p.m. at the beginning of runoff to 0.34 p.p.m. at the end of the runoff period. For the 96-hour treatment, atrazine concentrations at the beginning and end of runoff were 4.35 and 0.17 p.p.m., respectively.

The lower concentrations and losses where atrazine was applied for 96 hours as compared with 1 hour before the start of rain are to be expected. High surface soil temperatures, photodecomposition, and microbial degradation all contribute to breakdown of this herbicide under field conditions (Burnside, Fenster, *et al.*, 1963; Jordan, Day, *et al.*, 1964; Kearney, Sheets, *et al.*, 1964; McCormick and Hiltbold, 1966; Sheets and Danielson, 1960).

Under the conditions of this study, where atrazine was surface-applied to dry soil, volatilization and photodecomposition were probably the main pathways of loss. The soil temperature effect was likely the most important single factor contributing to the lower losses in washoff for the 96-hour treatment. Kearney, Sheets, *et al.* (1964) previously suggested that field atrazine losses by volatilization may be significant under high soil temperature conditions. In a laboratory study, they found that when atrazine was applied to several soils at 95° F., up to 40% was lost during a 72-hour period. Increasing the temperature to 113° F. almost doubled losses. In the present study, soil temperatures as high as 107° F. were measured at a 1-inch depth on some of the field plots. Soil surface temperatures were probably much higher.

The data show that atrazine was adsorbed by soil particles in the washoff material (Table I). Atrazine concentrations in the soil fraction were much higher than in the water fraction. At the initial sampling time, the atrazine soil to water concentration ratio was about 10 to 1. However, because relatively greater amounts of water were lost as compared with soil, greatest washoff losses of atrazine on a quantitative basis were associated with the water fraction (Figure 2). The total amounts lost in water were about 7 and 10 times greater than in the soil for the 1-hour and 96-hour treatments, respectively.

Differences between replications in atrazine concentrations and amounts in washoff were significant at the 0.01 probability level. Concentrations and losses for both the 1-hour and 96-hour treatments were lower during the first run (Table II). Temperature effects are suggested as the major cause of these differences. The first replication was run five days before the second. Both air and soil temperatures were higher during the days preceding and on the day of the first run.

The lower washoff losses from the first replication as compared with the second for the 96-hour treatment probably resulted because of greater field decomposition during the higher temperature period prior to rainfall. Temperature effects at the time of rainfall would also contribute to differences in atrazine content in washoff. Solubility of herbicides and adsorption by soil particles would both be influenced by temperature (Bailey and White, 1964). The difference observed between replications for the 1-hour treatment is probably more related to these phenomena than to decomposition losses.

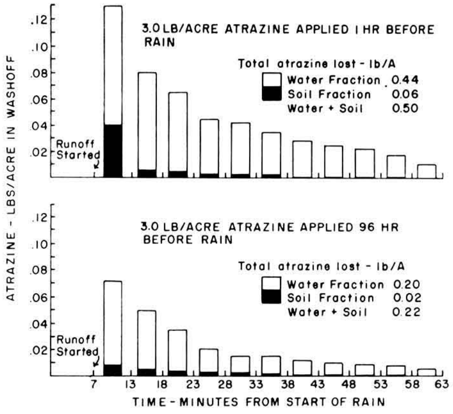

**Figure 2. Atrazine losses in washoff by time periods resulting from a 1-hour rain of 2.5 inches (fallow Cecil soil, 6.5% slope)**

Soil samples from field plots taken 24 hours after the test storm also showed lower atrazine concentrations for the 96-hour treatment as compared with the 1-hour treatment (Table III). Very little atrazine moved into the soil profile. Most was retained in the upper 3 inches of the soil profile. No measurable quantities were found below 6 inches. The 3.6-p.p.m. concentration in the 0- to 3-inch soil layer (approximately 1 million pounds of soil) for the 1-hour treatment indicates more atrazine was recovered than was applied. This probably was due to experimental error associated with the sampling procedure used.

The 1-hour rainfall of 2.5 inches used in this study is comparable to a 10-year frequency storm—i.e., one that can be expected to occur on an average of once every 10 years at Watkinsville, Ga. (Hershfield, 1961). Consequently, the total losses resulting from a storm of this magnitude should be considered as much greater than would normally be encountered. Not only is this size storm an infrequent event, but also it probably would not occur soon after field application of atrazine.

From results shown in Figures 1 and 2, atrazine losses to be expected from shorter duration or more frequent type storms can be determined. For example, a 1.25-inch rainfall in 30 minutes is a 1-year frequency storm (Hershfield, 1961). The cumulative loss from the first 33 minutes of runoff would be the total loss expected from this size storm. A short time interval between the end of rain and the end of runoff is normal. In the same manner, atrazine losses occurring in the first 13 minutes would correspond to those resulting from a 0.5-inch rainfall in 12 minutes. This size storm can be expected several times each year.

Table IV shows atrazine losses and concentrations in washoff for the various sizes of storms mentioned above. For all of the storms, both atrazine concentrations and amounts lost were much lower where atrazine was field-applied 96 hours before rain as compared with the 1-hour treatment. Atrazine losses increased with storm size, but the average concentration decreased. This was because the greater amounts of runoff from the larger storms caused a dilution of the atrazine. The greatest atrazine loss in washoff, 0.50 pound per acre, resulted

Table I. Atrazine Concentrations (P.P.M.) in Washoff during the Runoff Period from Field Plots Treated 1 and 96 Hours before Start of Rainfall

| | 1 Hour before Rain | | | 96 Hours before Rain | | |
|---|---|---|---|---|---|---|
| Time of Rain, Min. | Total washoff | Water fraction only | Soil fraction only | Total washoff | Water fraction only | Soil fraction only |
| 7 | 10.34 | 8.08 | 88.0 | 4.35 | 3.76 | 40.4 |
| 13 | 3.82 | 3.55 | 15.7 | 1.77 | 1.66 | 9.1 |
| 18 | 2.30 | 2.19 | 6.4 | 1.09 | 1.04 | 5.1 |
| 23 | 1.68 | 1.62 | 3.5 | 0.73 | 0.69 | 3.1 |
| 28 | 1.29 | 1.25 | 2.4 | 0.57 | 0.54 | 2.3 |
| 33 | 1.04 | 1.01 | 1.8 | 0.45 | 0.42 | 1.7 |
| 38 | 0.86 | 0.83 | 1.4 | 0.36 | 0.34 | 1.5 |
| 43 | 0.71 | 0.69 | 1.1 | 0.27 | 0.25 | 1.2 |
| 48 | 0.60 | 0.59 | 0.9 | 0.23 | 0.21 | 1.0 |
| 53 | 0.50 | 0.49 | 0.7 | 0.20 | 0.24 | 0.9 |
| 58 | 0.41 | 0.40 | 0.6 | 0.18 | 0.17 | 0.8 |
| 63 | 0.34 | 0.34 | 0.5 | 0.17 | 0.16 | 0.8 |

from the 10-year frequency storm coming 1 hour after the atrazine field application. Losses from the 1-year frequency storm were about 25% lower than losses from the 10-year frequency storm.

Atrazine loss from the 1.25-inch rain, 12.0% of that applied for the 1-hour treatment, is almost identical to that reported by Barnett, Hauser, *et al.* (1967) for a butylether ester form of 2,4-D. Using the same size storm and under similar conditions, they reported 2,4-D losses of 13%. This suggests that these two herbicides are similar in their susceptibility to loss by washoff from agricultural land.

From a practical standpoint, atrazine losses and concentrations shown for the 0.5-inch storm would be most realistic (Table IV). A storm of this size is classified as one that can be expected to occur on an average of three times a month during April, May, and June at this location (Miller and Frederick, 1966). The atrazine losses in washoff resulting from this size storm were about 25% of those from the 2.5-inch rain. Also, several days, rather than 1 hour, probably would lapse between the time of atrazine application and a rainfall occurrence. Therefore, the losses shown for the 0.5-inch storm and the 96-hour treatment probably represent the more frequent condition that would be encountered in the field. In this case, 2% or 0.06 pound per acre of the applied herbicide was lost in washoff.

The concentrations and losses reported herein relate to washoff as it immediately leaves a specific field site. Soil and water conservation practices such as terracing would prevent much of the washoff from leaving a field. Furthermore, as Barnett, Hauser, *et al.* (1967) pointed out, complete watersheds would seldom be treated, and washoff from treated areas would be diluted by runoff from untreated areas. Deposition into streams and ponds would result in further dilution. For example, if a 0.5-inch rain resulted in atrazine losses of 0.06

Table II. Atrazine Content in Washoff as Related to Temperature Conditions and Replications

| Replication No. | Air Temp., ° F. | Soil Temp., ° F. | Atrazine in Washoff | |
|---|---|---|---|---|
| | | | P.p.m. | Lb./acre |
| ATRAZINE APPLIED 1 HOUR BEFORE RAIN | | | | |
| 1 | 88[a] | 105[b] | 1.10 | 0.41 |
| 2 | 74[a] | 80[b] | 1.67 | 0.60 |
| ATRAZINE APPLIED 96 HOURS BEFORE RAIN | | | | |
| 1 | 86[c] | 107[d] | 0.54 | 0.20 |
| 2 | 78[c] | 92[d] | 0.70 | 0.24 |

[a] Maximum air temperature recorded at nearby weather station on day of run.
[b] Soil temperature recorded at 1-inch depth just prior to run.
[c] Mean maximum air temperature recorded at nearby weather station for 4 days prior to run.
[d] Mean maximum soil temperature recorded at 1-inch depth for 4 days prior to run.

Table III. Atrazine Concentration (Parts per Million) at Two Soil Depths 24 Hours after a 2.5-Inch Rainfall of 1-Hour Duration

| | Atrazine Applied | |
|---|---|---|
| Soil Depth, Inches | 1 hr. before rain | 96 hr. before rain |
| 0–3 | 3.6 | 2.3 |
| 3–6 | 0.1 | 0.4 |

**Table IV. The Effect of Storm Size on Atrazine Losses in Washoff**

| | | | | Atrazine in Washoff | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Applied 1 hr. before rain | | | Applied 96 hr. before rain | | |
| Storm Size, Inches[a] | Rainfall Duration, Minutes | Soil Loss, Tons/Acre[b] | Water Loss, Inches[b] | Total lost, lb/acre | % lost | Av. concn., p.p.m. | Total lost, lb./acre | % lost | Av. concn., p.p.m. |
| 0.5 | 12 | 0.26 | 0.07 | 0.13 | 4.3 | 7.94 | 0.06 | 2.0 | 3.66 |
| 1.25 | 30 | 1.84 | 0.61 | 0.36 | 12.0 | 2.54 | 0.16 | 5.3 | 1.13 |
| 2.50 | 60 | 5.30 | 1.54 | 0.50 | 17.0 | 1.39 | 0.22 | 7.3 | 0.62 |

[a] Storm sizes of 0.5, 1.25, and 2.50 inches represent a relatively common, a 1-year frequency, and a 10-year frequency storm, respectively, for Watkinsville, Georgia.
[b] Average of losses on all plots.

pound per acre from a 50-acre field, the initial washoff concentration would be 3.66 p.p.m. (Table IV). If this amount of atrazine was completely transported and deposited in an average size pond in the Piedmont area of Georgia, having a volume of 2.7 million gallons (Thomson, Herrick, *et al.*, 1956), the dilution from the pond alone would decrease the concentration to about 0.1 p.p.m.

From present information concerning toxicity levels of this herbicide, concentrations of the above magnitude probably would not constitute a serious pollution hazard to fish or wildlife. Rats fed daily for 2 years with food containing 200 p.p.m. atrazine were comparable in every respect to controls (Knüsli, 1964). Other tests have shown that the minnow (*Phoxinus phoxinus*) is unharmed when exposed to atrazine concentrations of 0.5 p.p.m. for 48-hour periods (Vivier and Nisbet, 1965). On the other hand, the long-term impact of pesticide residues upon biological systems is not well understood, and the possibility exists that subtle effects not readily apparent may exist (Stroud and Callison, 1965). A detailed discussion of this subject is beyond the scope of this paper.

In actual practice, a number of factors will influence the amount of atrazine appearing in washoff, and losses could vary from those reported in this paper. The recommended application rate of atrazine (3 pounds per acre) was used in this study. Greater losses would be expected if higher rates were used (Barnett, Hauser, *et al.*, 1967). Storm size and intensity and soil temperature conditions will influence the degree of loss. Also, erosion and runoff will vary with different soils and slopes.

The results from this study indicate that atrazine is transported in small but significant amounts in washoff from field plots of Cecil sandy loam. At recommended application rates of this herbicide and under field and rainfall situations most likely to be encountered, atrazine losses in washoff from soils and slopes similar to those of this study would be expected to occur most commonly in amounts of less than 0.1 pound per acre in the first storm after the herbicide application. Losses in subsequent storms should be progressively less than this amount.

### *Acknowledgment*

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# Determination of Radiostrontium in Food and Other Environmental Samples

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■ Radiostrontium in environmental samples is separated from the other alkaline earths in an EDTA medium. Earlier methods using the ion-exchange technique were modified to permit analysis of large samples, to provide quantitative separation from calcium in the wide range of concentrations normally encountered, to recover strontium in high yield, and to accommodate multiple analyses. The sensitivity of the procedure is 0.1 pc. per gram of ash when samples are counted for 50 minutes in a low-background beta counter; the average strontium yield is 70%. Decontamination factors are $5 \times 10^4$ from calcium and at least $1 \times 10^4$ from major radionuclides in fallout other than barium. Barium decontamination is 130. A procedure for the analysis of the barium plus radium fraction is also given.

The classical separation of strontium from calcium by means of the greater solubility of calcium nitrate in strong nitric acid and in certain organic solvents (Hillebrand, Lundell, *et al.*, 1953; Willard and Goodspeed, 1936) has commonly been used to determine radiostrontium in environmental and biological samples (Porter, Augustine, *et al.*, 1965). Complete removal of calcium simplifies yield measurements and self-absorption calculations in determining the concentrations of the pure beta emitters, strontium-89, and strontium-90. The procedure, however, requires numerous steps, and the use of fuming nitric acid holds a degree of hazard. Alternate methods for separation have therefore been introduced (Beccu, 1964; Butler, 1965; Campbell, 1965; Sunderman and Townley, 1960). Especially effective is the complexing of calcium with ethylenediaminetetraacetic acid (EDTA) at a pH at which strontium is mostly cationic. Strontium is then sorbed on cation-exchange resin (Davis, 1959; Elfers, Hallbach, *et al.*, 1964; Farabee, 1958; Ibbett, 1967; Tsubota, 1965; Wade and Seim, 1961) or precipitated (Berak and Munick, 1961; Eakins and Gomm, 1966; Hunter and Mitchell, 1964), while the calcium remains in solution.

In one of the simpler procedures, strontium, barium, and radium are retained on a resin column and the calcium-EDTA complex and other contaminants pass through. Strontium is then selectively eluted to separate it from barium and radium. The technique has been demonstrated in tracer studies (Bouquiaux and Gillard, 1964; Davis, 1959; Duyckaerts and Lejeune, 1960) and applied to the analysis of urine (Farabee, 1958), bone (Wade and Seim, 1961), and a variety of environmental samples (Davis, 1961; Elfers, Hallbach, *et al.* 1964). The separation of strontium from calcium, however, occurs only within narrow pH ranges that depend critically on EDTA concentrations at equilibrium, and these, in turn, are affected by the amount of calcium that must be complexed. Groups of samples that contain a constant amount of calcium are easily analyzed, but variable amounts of calcium lead to difficulties. The problem has been minimized or eliminated in the past either by removing most of the calcium during pretreatment (Elfers, Hallbach, *et al.*, 1964) or by matching the EDTA concentration to the predetermined calcium content (Davis, 1961).

In the method described here, sufficient excess EDTA is provided to analyze samples with a wide range of calcium content without prior treatment or individual adjustment of EDTA concentration. Moreover, calcium is removed so effectively that strontium may be determined gravimetrically as the carbonate, even though the calcium-strontium ratio in the sample may exceed 1000 to 1. The strontium yield is consistently near 70%, and other radionuclides occurring in fallout do not contaminate the purified sample. Barium and radium can be determined as part of the same procedure. The procedure was tested with a variety of individual foods, mixed diets, bone, soil, vegetation, and biological specimens and has been used routinely for analyzing hundreds of mixed-diet samples.

The procedure begins with the alkaline carbonate fusion of sample ash plus carriers. After the insoluble carbonates and hydroxides are washed and dissolved, EDTA is added, and magnesium is precipitated as $H_2Mg\ EDTA . 6H_2O$ (Brunisholz, 1957). The ion-exchange separation is performed, and the eluted strontium is precipitated as the carbonate. Strontium yield is measured gravimetrically, and radiostrontium is measured with a low-background beta counter. Strontium-90 is distinguished from strontium-89 either by recounting the sample and computing strontium-89 decay and yttrium-90

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Table I. Effect of Hydrochloric Acid Concentration on Strontium and Barium Recovery

| | 1.4$M$ HCl | | 1.5$M$ HCl | | 1.6$M$ HCl | |
|---|---|---|---|---|---|---|
| Fraction | % Sr | % Ba | % Sr | % Ba | % Sr | % Ba |
| 0 to 60 ml. acid | 3 | <0.01 | 4 | <0.01 | 5 | <0.01 |
| 61 to 460 ml. acid | 68 | 0.3 | 78 | 0.7 | 82 | 1.5 |
| 600 ml. 4$M$ NaCl | 25 | 99.5 | 14 | 99.2 | 9 | 98.4 |
| Remaining on resin | <0.01 | 0.2 | <0.01 | 0.07 | <0.01 | 0.09 |

ingrowth (Velten, 1966) or by chemically separating yttrium-90 and counting it (Porter, Augustine, *et al.*, 1965). Barium and radium can be eluted as a separate fraction and precipitated as the chromate. Barium-140 is measured with a beta or gamma detector, total radium by alpha counting, and radium-226 by dissolving the chromate and counting radon-222 and daughters by an emanation procedure.

### *Theory*

The pH for separating strontium from calcium at a specific EDTA concentration in a very short cation-exchange column can be estimated from the stability constants of the EDTA complexes of the two ions (Anokhin, 1960). The stability constant, $K$, is defined by:

$$K = \frac{[CA^{-2}]}{[C^{+2}]\,[A^{-4}]} \qquad \text{(1a)}$$

where $[C^{+2}]$ represents the concentration of either calcium or stronium ions, $[A^{-4}]$ of the completely dissociated form of EDTA, and $[CA^{-2}]$ of either the calcium or strontium complex; all concentrations are assumed to be sufficiently low for activity coefficients to be unity. If the sum of all forms of EDTA in solution is written as $\Sigma A$, and $\alpha$ is the ratio of $[A^{-4}]$ to $[\Sigma A]$ at equilibrium, the ratio of complexed to uncomplexed calcium or strontium is:

$$\frac{[CA^{-2}]}{[C^{+2}]} = \alpha K\,[\Sigma A] \qquad \text{(2)}$$

The logarithm of $K$ is 8.6 for strontium and 10.6 for calcium (Sunderman and Townley, 1960); the value of $\alpha$ as a function of pH can be calculated from the four p$K$ values for the dissociation of the hydrogen forms of EDTA—2.0, 2.8, 6.2, and 10.3 at 25° C. (Schwarzenbach and Ackermann, 1947). The computed product of $\alpha K[\Sigma A]$ for strontium and calcium in 0.05 and 0.09$M$ EDTA are shown in Figure 1.

Figure 1 indicates that a desired distribution between complexed and uncomplexed ions may be achieved at a variety of EDTA concentrations by adjusting the pH. The lower and higher limits of EDTA concentration are set respectively by the amount of calcium and other cations that must be complexed and the solubility of EDTA. Because the distribution ratio responds so sensitively to changes in pH and EDTA concentration, it is desirable to control the pH by buffering and the EDTA concentration by maintaining either no excess at all or a large excess over the expected calcium concentration.

At the equilibrium concentrations of 0.05 and 0.09$M$ EDTA used in this procedure, Figure 1 shows that a pH near 4.1 provides high calcium and low strontium complexing. This value, however, is only the starting point for determining the most favorable pH for the separation. On the one hand, the resin does not retain all of the uncomplexed ions. On the other, the separation is undoubtedly improved by using a relatively long column rather than a batch process, and by the somewhat greater affinity of the Dowex 50W-X8 resin for strontium than for calcium (6.51 for strontium and 5.16 for calcium relative to 1.00 for lithium) (Bonner and Smith, 1957). The presence of other cations will also affect distribution of strontium and calcium between resin and solution and between uncomplexed and complexed ions. Whatever the result of these effects, under conditions leading to a high strontium yield the resin probably will retain several per cent of the calcium, so that additional calcium elution is needed.

The logarithm of $K$ for barium is 7.8 (Schwarzenbach and Ackermann, 1947), which suggests that this ion is even less effectively complexed than strontium. In tracer experiments, the order of elution from cation-exchange resin columns was calcium, strontium, barium, and radium (Duyckaerts and Lejeune, 1960).

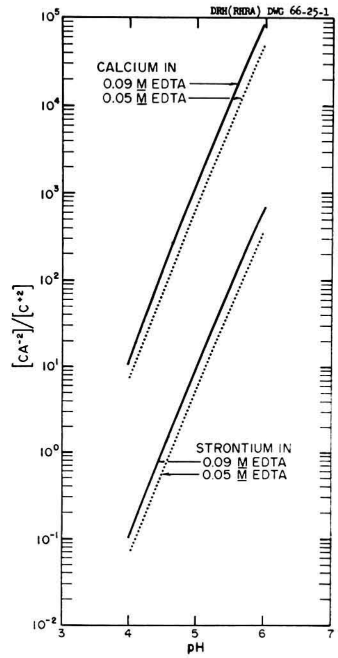

**Figure 1. Complexing of calcium and strontium computed as a function of EDTA concentration and pH**

## *Experimental*

**Reagents and Apparatus.** Dowex 50W-X8 (50- to 100-mesh) cation-exchange resin in sodium form.

A glass reservoir (1-liter separatory funnel) and a glass column (2.5-cm diameter) to contain 40-ml. resin.

Prepare resin by washing the column with 600 ml. of $4M$ sodium chloride solution and then with 200 ml. of distilled water. After use, regenerate by the same procedure.

Prepare strontium carrier (20 mg. of $Sr^{+2}$ per ml.) by dissolving 48.3 grams of anhydrous strontium nitrate in 900 ml. of water and 1 ml. of concentrated nitric acid, and dilute to 1 liter. Prepare barium carrier (5.0 mg. of $Ba^{+2}$ per ml.) by dissolving 9.50 grams of barium nitrate in 900 ml. of water and 1 ml. of concentrated nitric acid and diluting to 1 liter. Prepare 6% EDTA by dissolving 665 grams of disodium ethylenediaminetetraacetate dihydrate (mol. wt. 372.2) in 10 liters of water. Prepare pH 4.6 buffer by dissolving 200 grams of sodium acetate in 500 ml. of water, adding 385 ml. of glacial acetic acid, and diluting to 1 liter.

Check carriers for radioactive purity by evaporating and counting several 2-ml. aliquots. If the average count exceeds 0.2 c.p.m. above background in a low-background beta counter, the carrier should not be used.

**Procedure.** Place 10 grams of ash in a 250-ml. nickel crucible. Pipet 2 ml. of strontium and 1 ml. of barium carrier into the ash. Add 1 ml. of $2M$ calcium nitrate solution. Add 50 grams of sodium hydroxide pellets, mix, and fuse over a burner for 30 minutes. Slowly add 5 grams of anhydrous sodium carbonate, stir, and heat the clear melt for 30 minutes. Transfer the crucible from flame to cold-water bath to crack the mixture. Add 200 ml. of hot distilled water, and gently boil to disintegrate the fused mixture. Cool in ice bath, and then transfer to centrifuge tubes. Centrifuge, and discard supernatant solution. Wash the melt twice with 200-ml. portions of hot distilled water.

Dissolve the melt in 20 ml. ot $6N$ hydrochloric acid by boiling gently. Add 100 ml. of water. Filter. If insoluble residue (silica) is present, wash the residue twice with 100-ml. portions of water, and add wash solutions to filtered solution. Discard the residue. Add the filtrate to 500 ml. of 6% EDTA solution and adjust to pH 3.8 (pH meter) with approximately 10 ml. of $15N$ ammonium hydroxide. Stir vigorously for 75 minutes to precipitate magnesium salt of EDTA. Filter and

**Table II. Accuracy and Precision of Analyses**

| Radionuclide sample | No. of replicates | Radionuclide Concentration, Pc./Gram Ash | | Standard Deviation, % | |
|---|---|---|---|---|---|
| | | Actual[a] | Determined | Measured values | Counting only |
| $^{90}$Sr tracer[b] | 4 | 459 | 457 | ±5 | ±2 |
| environmental[c] | 16 | 19 | 16 | ±12 | ±10 |
| $^{140}$Ba tracer[b] | 3 | 33,000 | 33,300 | ±5 | ±0.6 |
| environmental[c] | 2 | 48 | 46 | ±11 | ±3 |
| $^{226}$Ra tracer[b] | 8 | 10.9 | 10.0 | ±6 | ±2 |
| environmental[c] | 16 | 1.2 | 1.1 | ±9 | ±4 |

[a] In tracer study, amount of added tracer; in environmental sample, value determined by previously used procedure (Porter, Augustine, *et al.* 1965).
[b] Diet sample.
[c] Grass sample.

**Table III. Distribution of Fallout Radionuclides at Various Steps in the Procedure**

| | Count Rate, C.P.M. (% of Added Tracer) | | | | | | |
|---|---|---|---|---|---|---|---|
| Radionuclide | Added | Fusion Supernatant and Wash | EDTA Effluents | 60 Ml. HCl | Residue on Resin | $SrCO_3$ Filtrate and Washes | $SrCO_3$ |
| $^{95}$Zr + $^{95}$Nb | 1,027,000 | 203,000 | 805,000 | 1,395 | 10,890 | 4,743 | 140 |
| | (100) | (19.8) | (78.4) | (0.14) | (1.06) | (0.46) | (0.01) |
| $^{106}$Ru | 903,200 | 364,700 | 530,800 | 237 | 6,977 | 455 | 21 |
| | (100) | (40.4) | (58.8) | (0.03) | (0.77) | (0.05) | (0.002) |
| $^{137}$Cs | 1,045,000 | 1,044,000 | 0 | 0 | 1,000 | 0 | 0 |
| | (100) | (99.9) | (<0.001) | (<0.001) | (0.095) | (<0.001) | (<0.001) |
| $^{91}$Y | 879,400 | 771 | 878,400 | 27 | 123 | 0 | 28 |
| | (100) | (0.08) | (99.9) | (0.003) | (0.012) | (<0.001) | (0.003) |
| $^{140}$Ba | 349,600 | 3,226 | 0 | 0 | 343,700 | 0 | 2,571 |
| | (100) | (0.92) | (<0.001) | (<0.001) | (98.3) | (<0.001) | (0.73) |
| $^{90}$Sr | 313,400 | 416 | 1,900 | 6,435 | 58,600 | 2,956 | 243,000 |
| | (100) | (0.14) | (0.60) | (2.05) | (18.7) | (0.94) | (77.5) |
| $^{144}$Ce | 937,300 | 3,960 | 932,800 | 66 | 459 | 368 | 10 |
| | (100) | (0.42) | (99.5) | (0.007) | (0.04) | (0.04) | (0.001) |
| $^{54}$Mn | 1,039,000 | 329,500 | 708,600 | 24 | 679 | 227 | 0 |
| | (100) | (31.7) | (68.2) | (0.002) | (0.05) | (0.02) | (<0.001) |
| $^{131}$I | 1,123,000 | 1,117,000 | 5,190 | 54 | 738 | 0 | 78 |
| | (100) | (99.6) | (0.30) | (0.003) | (0.04) | (<0.001) | (0.004) |

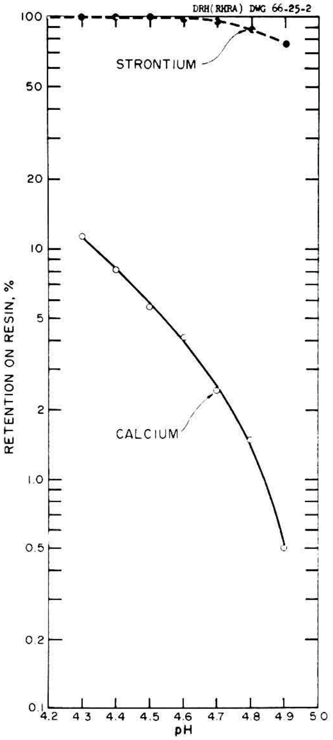

**Figure 2. Retention of strontium and calcium on Dowex 50W-X8 resin as a function of pH**

**Food sample in 1 liter of 3% EDTA; 40 ml. of resin in 2.5-cm. (diameter) column**

adjust filtrate to pH 4.6 (pH meter) with approximately 13 ml. of 15*N* ammonium hydroxide. Add 20 ml. of buffer solution (pH 4.6) and dilute to 1 liter.

Let the solution flow through the resin column at 20 ml. per minute. Stop the flow when just enough solution remains to cover the resin. Combine 200 ml. of 6% EDTA solution and 400 ml. of water, adjust to pH 5.1 (pH meter) with 6*N* ammonium hydroxide, place in reservoir, and let flow at 20 ml. per minute. Record time at the end of elution as the beginning of yttrium-90 ingrowth. Wash the column with 200 ml. of water at a flow rate of 20 ml. per minute. Discard all effluents. Place 460 ml. of 1.5*N* hydrochloric acid in reservoir, and elute at flow rate of 8 ml. per minute. Discard the first 60 ml. of effluent. Collect the next 400 ml., which contains the strontium fraction. Regenerate the resin with 600 ml. of 4*M* sodium chloride and 200 ml. of water. If the barium-radium fraction is to be analyzed, collect sodium chloride effluent.

To the strontium fraction, add 200 ml. of concentrated ammonium hydroxide, and stir with a magnetic stirrer. Slowly add 10 ml. of 3*N* sodium carbonate solution, and stir 30 minutes. Collect strontium carbonate on tared membrane filter. Wash with three 10-ml. portions each of water, 95% alcohol, and diethyl ether. Weigh and count radiostrontium in low-background beta counter.

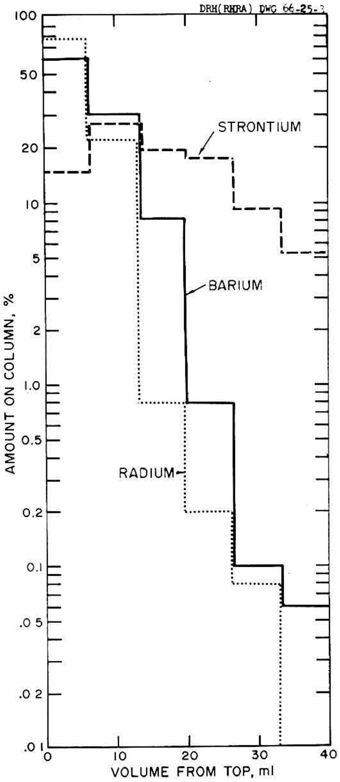

**Figure 3. Distribution of strontium, barium, and radium on resin column**

**Tracers from food sample in 1 liter of 3% EDTA solution; 40 ml. of Dowex 50W-X8**

To the barium-radium fraction, add 4 ml. of strontium carrier, 20 ml. of 6*N* sodium hydroxide, and 10 ml. of 3*N* sodium carbonate. Stir and filter. Wash precipitate with 20 ml. of water. Dissolve the precipitate on the filter with 1 ml. of 6*N* nitric acid, and wash the filter with 20 ml. of water, collecting the solution in glass centrifuge tube. Neutralize with approximately 1 ml. of 6*N* ammonium hydroxide, and add 5 ml. of buffer solution (pH 4.6). Add 1 ml. of 3*N* sodium chromate while stirring to precipitate barium and radium chromate. Collect on tared membrane filter. Wash with three portions each of water, 95% alcohol, and diethyl ether. Weigh, and count barium-140 and beta-emitting radium daughters in low-background beta counter.

### *Results and Discussion*

Initial tests with radioactive calcium and strontium tracers were performed to select the EDTA concentrations, pH, and resin volume for high strontium yield and effective calcium decontamination. Ten-gram samples of ash, representing 100 to 5000 grams of moist food, were analyzed to obtain readily measurable amounts of strontium-90 in actual samples. The test sample—a child's diet selected after a survey of radionuclides in institutional diets—contained 800 mg. of calcium and 1.5 mg. of strontium per 10 grams of ash. The procedure was later tested with individual foods that contained between 10 and 1500 mg. of calcium and between 0.2 and 4 mg. of strontium.

The preparational steps, fusion, washing, dissolution, and filtration, converted strontium, barium, and radium into carbonates and eliminated most of the alkalies, interfering anions such as sulfates and phosphates, and silica. Silica did not commonly interfere with the analysis of foods, but it clogged the resin column in soil and vegetation samples. Strontium losses from the carbonate precipitate to the supernatant solution were well below 1% when calcium nitrate was added as indicated; with less than 100 mg. of calcium, strontium losses reached 15%, hence calcium was added to all samples. Magnesium was precipitated at pH 3.8 as the EDTA salt.

A 3% solution of EDTA (0.089*M*) was most suitable for complexing calcium. At lower EDTA concentrations, calcium decontamination was affected too strongly by difference in the calcium content of the sample. Thus, 10 mg. of calcium per sample did not affect the EDTA concentration, 800 mg. reduced it to 0.069*M*, and 1500 mg. to 0.051*M*. As shown in Figure 1, the largest calcium difference has the same effect as a change in pH of 0.1.

The highest pH value at which strontium was almost completely retained on the resin was 4.7 (Figure 2). To provide a margin of safety, pH 4.6 was selected for routine use. Buffer solution was added to the influent (Davis, 1961) to limit the usual rise of 0.3 in pH. within the resin column to 0.1 or less. At this controlled pH, strontium losses were 2%; 4% of the initial amount of calcium remained.

The retained calcium was eluted with 600 ml. of a 2% solution of EDTA (0.059*M*) at pH 5.1. The concentration of uncombined EDTA was thus approximately the same as in the food solution, but adjusted to a higher pH for more effective calcium decontamination. The strontium loss in this step was 2%. Only 0.16 ± 0.08 ($1\sigma$) mg. of calcium contaminated the strontium after the elution.

Optimum column volume and flow rate were determined from the distribution of strontium along the resin column. A 40-ml. column had the distribution shown in Figure 3 at a flow rate of 20 ml. per minute. An additional 7.5 ml. of resin would have increased strontium retention by 0.5%; removal of 7.5 ml. would have decreased retention by 5%. The flow rate of 20 ml. per minute represents a cross-sectional rate of 4.1 ml. per minute-cm$^2$. Strontium analysis can be performed at flow rates four times as great without appreciable additional loss, but higher contamination by barium and radium made flow rates above 20 ml. per minute undesirable. Increased resolution of the strontium and barium fractions on the resin at lower flow rates, on the other hand, was not sufficiently great to counterbalance the advantages of more rapid analysis.

Tests with radioactive barium and radium tracers showed total losses to be less than 1% during initial treatment, retention on the resin column, and elution of residual calcium. After the calcium elution, 99% of the barium and radium is concentrated on the upper half of the resin column (Figure 3).

To separate strontium from barium and radium, 460 ml. of 1.5*M* hydrochloric acid is passed through the resin column. As shown in Table I and Figure 4, most of the strontium is eluted with 0.7% of the barium and 0.4% of the radium. The first 60 ml. of effluent is discarded because EDTA adsorbed on resin (Davis, 1961) is eluted in this portion and interferes with subsequent strontium precipitation. Four per cent of the initial strontium is discarded with the first 60 ml., 78% is recovered in the next 400 ml., and 14% remains on the resin column. The importance of maintaining the hydrochloric acid concentration within ± 0.1*N* to obtain high strontium yield and low barium contamination is shown in Table I.

Strontium is precipitated as a carbonate from the neutralized effluent. The uniform mixing provided by magnetic stirring appears necessary to form an easily filtrable precipitate. No more than 10 ml. of 3*N* sodium carbonate should be used because of calcium impurities; 10 ml. of solution prepared from reagent (ACS) grade may contain as much as 0.2 mg. of carbonate-insoluble calcium and magnesium salts. The indicated excesses of ammonium hydroxide and sodium carbonate are required for high strontium yield. An average of 2% of the strontium is lost by filtering. The average over-all yield in 100 determinations of a variety of food samples was 70 ± 3 ($1\sigma$) %.

The gravimetrically measured yield is systematically high because of the presence of stable strontium in all foods. The range of stable strontium in foods, 0.2 to 4 mg. per 10-gram sample of ash, means that the yield is overestimated by 0.5 to 10%. The resulting underestimation of radiostrontium content is not serious for radiological health purposes; it may be minimized by assuming an average strontium content in the sample—say 1 mg.—or eliminated by measuring the actual strontium content (Elfers, Hallbach, *et al.* 1964; Strong, Rehnberg, *et al.* 1966).

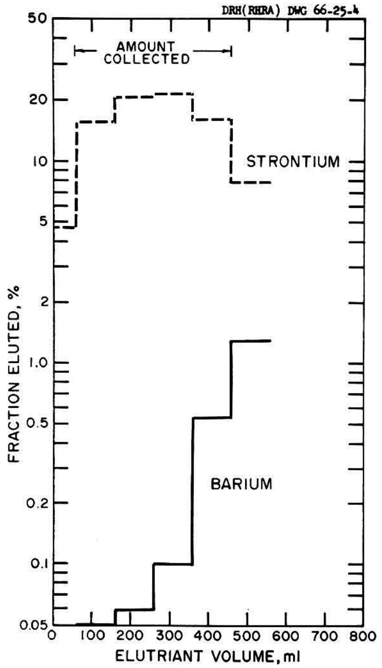

**Figure 4. Elution of strontium and barium from 40-ml. Dowex 50W-X8 resin column by 1.5*M* HCl**

The procedure was tested with tracer at high radioactive strontium concentrations to obtain precise values, and at environmental concentrations under actual conditions. As shown in Table II, results agreed within the standard deviation of replicate analyses with analyses performed by the previously used method (Porter, Augustine, *et al.*, 1965). The standard deviation at high radiostrontium concentrations, reflecting mainly analytical error, was 5%. At environmental concentrations, the average value was 16 pc. and the standard deviation was 2 pc. This standard deviation was largely attributable to the counting error at counting times of 50 minutes, a counting efficiency of 40%, and a background of 1 c.p.m. Under these conditions, the minimum detectable limit ($3\sigma$ value) for a 10-gram sample was 0.1 pc. per gram. One analyst processed on the average 4 samples in 8 hours.

**Table IV. Types of Samples Analyzed**

| Sample | Ash Content, Grams/Kg. Moist Wt. | Calcium, Grams/ 10 G. Ash | Stable Strontium, Mg./10 G. Ash | $^{90}$Sr, Pc./10 G. Ash |
|---|---|---|---|---|
| Oranges | 4.8 | 0.75 | 3.96 | 4.6 |
| Bread | 19.8 | 0.50 | 0.99 | 12.0 |
| Evaporated milk[a] | 15.5 | 1.64 | 1.43 | 30.6 |
| Bran cereal | 77.2 | 0.12 | 0.74 | 34.3 |
| Eggs | 7.7 | 0.61 | 1.40 | 3.2 |
| Oleomargarine | 21.3 | 0.09 | 0.19 | 2.7 |
| Brewed coffee | 2.3 | 0.15 | 1.33 | 2.3 |
| Instant coffee | 106.0 | 0.17 | 1.20 | 3.0 |
| Pork | 8.5 | 0.14 | 0.39 | 1.3 |
| Spinach | 15.0 | 0.46 | 1.43 | 12.4 |
| Apples | 3.0 | 0.12 | 1.29 | 6.0 |
| Beef | 6.9 | 0.08 | 0.36 | 2.8 |
| Potatoes | 9.4 | 0.05 | 0.73 | 4.1 |
| Milk | 7.3 | 1.60 | 1.07 | 25.3 |
| Institutional diet composite | 10.0 | 0.4–1.2 | 0.5–2.0 | 16.0 |
| Bone[b] | 164.9 | 3.74 | 3.80 | 75.4 |
| Vegetation | 22.4 | 1.2 | 3.08 | 36.0 |

[a] 5 grams of evaporated-milk ash used for analysis.
[b] 3 grams of bone ash used for analysis.

Decontamination from the major radioactive contaminants in environmental samples was better than 10,000, as shown in Table III, except from barium, which showed a decontamination factor of 130. Most contaminants are separated in the ion exchange step; iodine, cesium, and ruthenium, however, are removed to a great extent by washing the fusion mixture; and small amounts of ruthenium, zirconium plus niobium, and manganese are finally removed in filtering and washing the strontium carbonate. As shown in Figure 4, barium decontamination could be improved by sacrificing strontium yield. In the absence of barium-140, the strontium yield could be increased 8% by eluting with an additional 100 ml. hydrochloric acid, and increased 14% with an additional 400 ml.

If barium and/or radium in the sample are to be analyzed, they can be precipitated in the sodium chloride elutriant by coprecipitation with strontium carbonate. A subsequent precipitation of barium chromate at pH 4.6 removes 99.9% of the radiostrontium and strontium carrier, with a 6% loss of barium and radium. Final barium and radium yields are 88 ± 2%. The barium chromate precipitate weighs only 8 mg. (3 mg./cm.$^2$ on a 2.6-cm.$^2$ deposition area) and the radium and daughters may be alpha counted with minimal self-absorption losses. Accuracy and precision of this barium and radium analysis are given in Table II.

The procedure described here was applicable to all of the samples listed in Table IV. Silica was an interfering substance in soil, silt, and grass, but was effectively removed by filtering the fusion mixture dissolved in hydrochloric acid. Large amounts of calcium have the greatest effect on the samples; for foods, however, strontium yield and calcium decontamination remained unaffected by changes of calcium content ranging from 10 to 1600 mg. Yield and decontamination began to decrease when added calcium brought the total calcium content above 3 grams, and were unsatisfactory for calcium contents above 3.5 grams. Magnesium in amounts above 0.5 gram per 10 grams of ash combined with calcium to interfere, in that magnesium removed EDTA from solution by precipitating an insoluble EDTA salt at pH 3.8. The sample size must therefore be reduced in the presence of large amounts of calcium and magnesium.

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**COMMUNICATION**

# Ammonia in Auto Exhaust

**John H. Harkins[1] and Stephen W. Nicksic[2]**
Chevron Research Co., Richmond, Calif. 94802

■ Ammonia in the exhaust from a laboratory V-8 engine was measured to see if the amount was sufficient to account for ambient levels. Exhaust samples were cold-trapped from an engine operated at both steady-state conditions and over the California State Motor Vehicle Pollution Control Board traffic cycle. The concentration in the condensate ranged from 1 p.p.m. at idle to 6 p.p.m. at 50 m.p.h. road load and averaged 2.2 p.p.m. over the entire traffic cycle. The presence of nitrogen-containing detergent additives or lead antiknock compound in the fuel did not affect the amount of exhaust ammonia. On the basis of the data, up to 10% of ammonia in the atmosphere can be accounted for by ammonia discharged from motor vehicles.

Ammonia is found in the atmosphere of urban communities in concentrations up to 0.2 p.p.m., with average concentrations of 0.02 p.p.m. (Jacobs, 1960). Ammonia results from the combustion of fuels as well as other reactions and natural sources. Although ammonium salts were suspected of causing some of the respiratory irritation in the Donora, Pa., episode in 1950 (Faith, 1959), ammonia is considered of limited importance as an atmospheric contaminant. It is reasonable to expect ammonia to neutralize, partially at least, acidic airborne constituents such as $SO_2$ and $SO_3$, and their hydrated forms, with consequent reduction in the irritant qualities of each. This neutralizing function of $NH_3$ in atmospheric chemistry was of interest to the authors in their studies on the role of $SO_2$ in atmospheric visibility reduction (Harkins and Nicksic, 1964, 1965). Because of the paucity of data on the concentration of ammonia in auto exhaust, a program was run to measure exhaust ammonia emitted from a laboratory engine.

## *Experimental*

**Equipment and Procedure.** The tests were run on a laboratory 1956 Oldsmobile V-8 engine at both steady state conditions and over the California Motor Vehicle Pollution Control Board cycle (217 West First Street, Los Angeles, Calif. 90012).

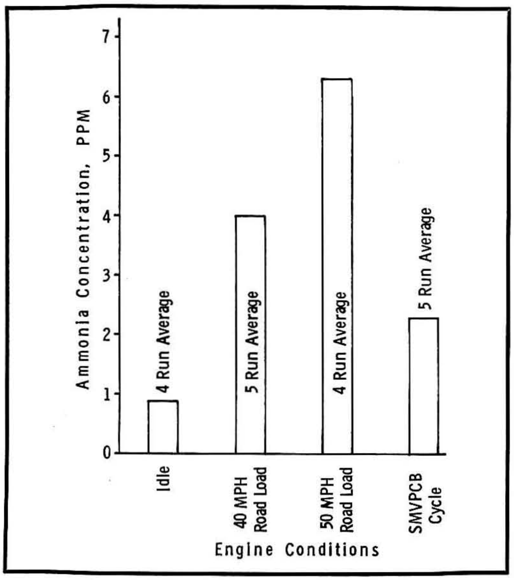

**Figure 1. Ammonia in automobile exhaust gas**

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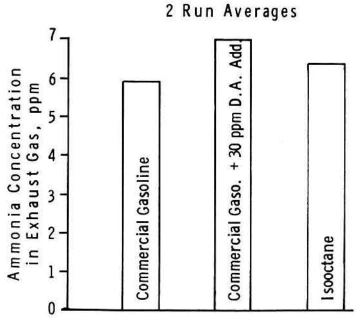

**Figure 2. Effect of fuel composition on ammonia concentration in exhaust gas–engine conditions: 50 m.p.h. at road load**

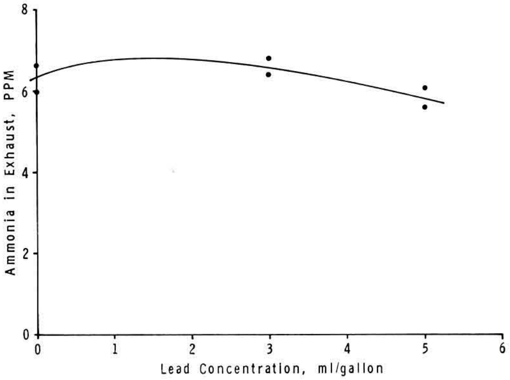

**Figure 3. Effect of Pb concentration on ammonia in exhaust—engine conditions: 50 m.p.h. at road load**

The samples for ammonia determination were collected at the outlet of the exhaust manifold by cold trapping a typical exhaust sample. The trap temperature was −5° C., and very little ammonia was found in a second trap in series when one was used. Ammonia was determined by an evolution-titration procedure, as in the familiar Kjeldahl method. Over-all reproducibility was within ±15% of the averages reported in Figure 1.

**Results.** Figure 1 is a bar graph showing the ammonia concentration in auto exhaust at three steady state conditions and over the California cycle. This figure shows that the ammonia concentration ranges from about 1 p.p.m. at idle (600 r.p.m.) to 6 p.p.m. at 50 m.p.h. (1800 r.p.m.) road load. The average concentration on the state cycle was 2.2 p.p.m. The procedure employed to measure ammonia will include volatile amines or the ammonia resulting from the combustion of nitrogen-containing additives. Although it seemed unlikely that organic nitrogen compounds would contribute to exhaust ammonia, the possibility was investigated because the test fuel contained a nitrogen-containing additive.

Figure 2 is a bar graph showing the effect of fuel composition on ammonia concentration in exhaust gas. This figure shows that within experimental error there is no difference in exhaust ammonia between commercial gasoline, iso-octane (no nitrogen compounds in the fuel), and commercial gasoline plus 30 p.p.m. of a carburetor detergent action (DA) additive (*N*-aminoalkyl acid amide, 7.6% N).

This suggests that the ammonia is formed during the combustion process, probably by direct reaction of hydrogen and nitrogen atoms. If this is the case, lead concentration of the gasoline might possibly have a catalytic effect on the formation of ammonia. Figure 3 is a plot of the concentration of ammonia in exhaust as a function of the lead concentration. This figure shows that at concentrations up to 5 ml. per gallon, lead has no effect (within experimental error) on the ammonia content of the exhaust.

### *Discussion*

The tests showed that ammonia is present in gasoline engine exhaust in concentrations up to 6 p.p.m. and suggests that the ammonia is formed during the combustion process. If we assume that exhaust ammonia is dispersed in the atmosphere in the same way as carbon monoxide, use a 1000 to 1 exhaust dilution typical of dense city traffic conditions (Begeman, 1962), and use the average value of 2.2 p.p.m. ammonia in exhaust over the California cycle, we can account for 10% of the ammonia in the atmospheres of urban communities such as Los Angeles. (In less populated areas, exhaust dilutions would be greater than 1000 to 1, but sampling of atmospheric concentrations of contaminants such as ammonia is usually carried out in urban areas.) Therefore, apparently auto exhaust is not a major source of atmospheric ammonia.

Ethylene dibromide and ethylene dichloride used as lead scavengers burn to yield HBr and HCl which could neutralize (and probably do) some of the ammonia, as evidenced by the findings of Hirschler *et al.* (1957) showing mixed $PbCl_2$–$NH_4Cl$ crystalline deposits in the exhaust train. The present data do not indicate whether exhaust ammonia is free or combined ammonia and, hence, do not necessarily reflect the ammonia available to neutralize acidic atmospheric gases. However, some atmospheric ammonia can be accounted for by the ammonia in auto exhaust. These tests were run on an engine without an exhaust emission control system. Before any firm conclusions can be drawn, more data are needed on both the effect of emission control devices on ammonia production and on current atmospheric ammonia levels.

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# Public policy on pesticides modified by economic factors

**The Pesticide Problem: An Economic Approach to Public Policy.** J. C. Headley and J. N. Lewis. xvii + 141 pages. Johns Hopkins Press, Baltimore, Md. 21218. 1967. $3.50, paper. *Daniel MacDougall is Director of Research and Development, Chemagro Corporation, Kansas City, Mo. 64120*

### *By Daniel MacDougall*

Since Rachel Carson's impassioned attack on pesticides in *Silent Spring,* there has been a continuing controversy on the merits and demerits of chemical control agents for pests. In an atmosphere charged with emotion, it is difficult to obtain a coldly logical evaluation of the facts. Thus, the appearance of the book, *The Pesticide Problem: An Economic Approach to Public Policy,* is a welcome change from many of the earlier publications on this subject.

The authors have provided a classical economic framework which they suggest could be used for the evaluation of the total social impact of pesticides. They point out that "the controversy surrounding the pesticide question is based on the lack of knowledge in four areas within this framework." These are "the positive benefits resulting from incremental changes in the output of agriculture and forestry, the magnitude of the external costs of pesticide usage, a means of placing values on the physical external costs, and the substitution rates of other inputs such as land, labor, and fertilizer for pesticides." The above excerpt is sufficient to illustrate the problems which the reader who is not thoroughly familiar with technical economic writing may have in properly comprehending this book.

This review of actual data on the benefits of pesticides is excellent, although the text was probably prepared some time ago and there are considerable amounts of more recent pertinent data now available. However, these do not alter the basic picture regarding the effects of pesticides on the amount and quality of agricultural production or their role in the prevention of disease. The authors emphasize the importance of pesticides in releasing labor resources for other uses and suggest that in some cases this may be their primary beneficial effect.

#### Toxic effects

Evidence for problems in pesticide use is also reviewed. It is pointed out that the principal hazard to human health is from occupational exposure. The authors suggest these people should be watched very carefully for subtle toxic effects in order to obtain leads as to possible effects from long term low level exposure of the population as a whole. On the other hand, it is emphasized that there are no known instances of harm to any person from eating pesticide-treated food when the treatment was made in accordance with the label. There are some isolated instances of illness occurring from eating food which was treated in a manner contrary to label instructions.

Similarly, there are no recorded instances of seizure of crops following the use of pesticides in accordance with instructions. Usually excess residues have resulted from gross disregard of the label directions for use. In the great majority of foods analyzed by the various monitoring agencies residues are far below the permitted tolerance levels. Furthermore, there is no evidence of an increase in the residue levels in man in the U.S. over the past several years.

The accidental poisoning situation the United States is also reviewed. In the years 1956 and 1961, children under 10 years of age accounted for over 50% of the deaths due to pesticide. Also even in 1961 over 50% of the deaths were due to chemicals older than DDT. The number of deaths of children is much greater in this country than in England or Sweden where fewer than 10% of the deaths attributed to pesticides were of children. This undoubtedly reflects rather careless handling of these toxic compounds by a significant fraction of the American population.

The inconsistency of public policy in the United States regarding the threshold and no threshold hypotheses is pointed out. Only in the case of possible carcinogens is the "no threshold" hypothesis accepted. The authors conclude that there is "no empirical evidence to support this" position and "imposing a zero tolerance simply because one type of risk is involved, while non-zero tolerances are set in other types of health risk, regardless of the magnitude of the risk and of the outcome, is patently inconsistent."

#### Fish and wildlife

The possible effects of pesticides on fish and wildlife are reviewed. It is emphasized that in this area it is exceedingly difficult to obtain data which illustrate the true effects of pesticides. Possible harmful effects such as decreased reproduction, increased stress in times of disease, and starvation are listed. However, the authors point out in an unbiased evaluation of effects of pesticides on wildlife that minimum mortality of fish, birds, and other wildlife, due either to intoxication with pesticides or deprivation of food sources, is not necessarily the objective. Initial mortality may sometimes have little permanent effect on wildlife populations because of the capacity of the species for regeneration. In addition, mortality caused by pesticides may merely hasten losses of wildlife which would eventually occur from other causes.

In summarizing the situation the authors conclude the following:

- The diversity of materials used as pesticides is increasing.
- The total quantity of materials has increased since 1939.
- The trend has been away from the arsenicals toward the chlorinated hydrocarbons, the organophosphorus compounds, and the carbamates.
- The use of herbicides is growing rapidly.
- Pesticides in agriculture are possibly very productive in terms of output increases and resource savings.
- Effects on human health are uncertain with possible benefits from control of disease-bearing insect vectors weighed off against known hazards as well as potential hazards.
- There is uncertainty concerning the balance of gains and losses with respect to effect of pesticides on fish and wildlife.

### Critique

Several of these conclusions are almost axiomatic. However, those concerning effect of pesticides on agricultural production and public health are not in keeping with the evidence presented in the text and one wonders how the authors reached these conclusions on the basis of the evidence presented.

My chief criticism of this book—other than the criticisms mentioned above, relative to the conclusions—is that it presents a theoretical framework which could be used for evaluating how the data necessary to answer the questions raised can ever be obtained. Surely the same sort of treatment could be given to many other factors in the environment—automobiles, plastics, tobacco, and the like. From this viewpoint, it appears that many of the questions raised are more hypothetical than practical. We question whether the magnitude of the problem warrants the efforts which would be required to evaluate the various economic questions raised. However, in general, the book presents a fairly balanced view of the overall pesticide situation.

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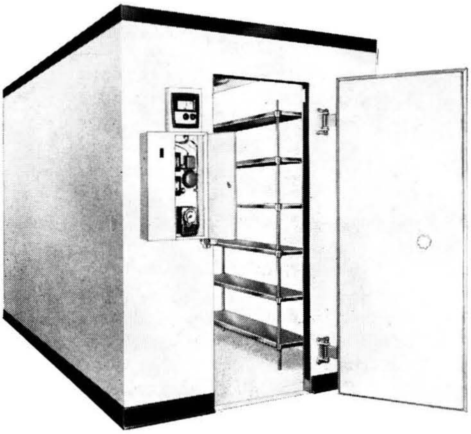
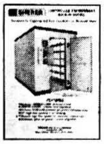
**Incineration of Solid Wastes.** Edited by Robert A. Fox. A symposium. 81 pages. Robert A. Fox, P.O. Box 607, Grand Central Post Office, New York, N. Y. 10017. 1967. $3.00, paper.

The volume contains the proceedings of the MECAR Symposium held March 21, 1967, in New York City. The proceedings present possible future alternatives to incineration or landfills for the disposal of solid wastes. Specific suggestions include improved packaging of foods, built-in ease of disposal of hard goods, feasible household garbage grinders, generating power from refuse, economically feasible ocean dumping, pyrolysis, and composting, as well as greatly improved incineration.

**Handbook of Chemistry: Revised Tenth Edition.** Compiled and edited by Norbert A. Lange and Gordon M. Forker. 1958





pages. McGraw-Hill Book Co., New York, N. Y. 10036. 1967. $12.00, hard cover.

The revision was made in response to the many recent changes in chemical concepts and technology, particularly the changes made to the atomic weights in the new international table, which is based on carbon-12. Many of the analytical factors and most of the formula weights of inorganic and organic compounds have been affected by the use of carbon-12 as a basis for all atomic weight calculations. Extensive changes have been made in descriptive tables of the elements, gravimetric factors and their logarithms, and fundamental physical constants.

**Pesticide Handbook—Entoma.** Compiled and edited by Donald E. H. Frear. 316 pages. College Science Publishers, State College, Pa. 16801. 1967. $3.00, paper; $4.50, hard cover.

Completely revised, the 1967 edition of this handbook lists the names, active ingredients, and manufacturers of nearly 10,000 insecticides, fungicides, herbicides, rodenticides, and other agricultural chemicals and equipment.

**Environment for Man: The Next Fifty Years.** Edited by William R. Ewald, Jr. A symposium. ix + 308 pages. Indiana University Press, Bloomington, Ind. 47401. 1967. $2.95, paper.

**Pest Management.** Bryan P. Beirne. 123 pages. Neill & Co., Ltd., Edinburgh, Scotland. 1967. $10.95, hard cover.

**Air Force Scientific Research Bibliography 1960. Vol. IV.** G. Vernon Hooker and others. xvi + 909 pages. U. S. Government Printing Office, Washington, D. C. 20402. 1966. $5.75, hard cover.

**Principles and Applications of Water Chemistry.** Edited by Samuel D. Faust and Joseph V. Hunter. A symposium. xv + 643 pages. John Wiley & Sons, Inc., New York, N.Y. 10016. 1967. $12.50, hard cover.

**The Orsanco Story: Water Quality Management in the Ohio Valley under an Interstate Compact.** Edward J. Cleary. xvi + 335 pages. Johns Hopkins Press, Baltimore, Md. 21218. $2.95, paper; $8.50, hard cover.

**Equilibrium Concepts in Natural Water Systems.** Advances in Chemistry No. 67. Edited by Robert F. Gould. A symposium. viii + 344 pages. American Chemical Society, Washington, D.C. 20036. 1967. $8.50, hard cover.

**1966 Saline Water Conversion Report.** U. S. Department of the Interior. xxiii + 340 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1967. $1.75, paper.

**Water Geology and the Future.** Water Resources Research Center, Indiana University (Bloomington). A symposium. 117 pages. Water Resources Research Center, Indiana University, Bloomington, Ind. 47405. 1967. No charge for limited distribution, paper.

**Water and America's Future.** Soil Conservation Society of America. A symposium. iv + 239 pages. Soil Conservation Society of America, 7515 N.E. Ankeny Road, Ankeny, Iowa 50021. 1967. $5.00, paper.

**Index to Air Pollution Research.** Nancy I. Miller. iv + 111 pages. Center for Air Environment Studies, Pennsylvania State University, University Park, Pa. 16802. 1967. $1.25, paper.

**Estuaries.** Publication No. 83 of the American Association for the Advancement of Science. Edited by George H. Lauff. A symposium. xv + 757 pages. American Association for the Advancement of Science, Washington, D.C. 20005. 1967. $27.00 ($24.00 to AAAS members), hard cover.

**Economic Costs of Air Pollution: Studies in Measurement.** Ronald G. Ridker. xiii + 215 pages. Frederick A. Praeger, Publishers, New York, N.Y. 10003. 1967. $13.50, hard cover.

**Dangerous Air.** Lucy Kavaler. 143 pages. John Day Co., New York, N.Y. 10036. 1967. $3.95, hard cover.

**Water Measurement Manual. Second Edition.** U.S. Department of the Interior. xix + 329 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1967. $2.50, hard cover.

# NEW PRODUCTS DIGEST

### Sampling Devices for Air Pollution

*A newly formed company provides portable units for sampling air pollutants. The portable air sampler is a precision built bubbler apparatus for collecting samples for the analysis of sulfur dioxide, oxidants, oxides of nitrogen, carbon monoxide, and the like. It features precision flowmeters and a high volume vacuum pump. The portable meteorological measuring system determines wind velocity and direction at a realistic height, not influenced by local ground events. It converts almost any car or van into a portable observation station. The third item provides shelving and racks for the measuring units. The latter is easily installed in any type of van and is customized to meet special requirements. Air Sampling Systems, Inc.* **60**

### Organic Carbon Analyzer

Model 915 analyzer determines, within 2–4 minutes, both total carbon and total inorganic carbon content, calculating total organic carbon (TOC) by difference. A choice of analysis ranges—from 0–50 and 0–4000 mg. organic carbon/l. sample—is available. The three-part unit consists of a TOC analysis unit with furnaces, a Beckman IR-215A infrared analyzer, and a strip-chart recorder. Beckman Instruments, Inc. **61**

### Automatic Liquid Sampler

Constructed of corrosion resistant aluminum alloy, this liquid sampler automatically obtains a dozen 16-oz. samples of contaminated water or sewage effluent over a predetermined, fixed period of time (at ½, 1, or 2 hour intervals). Testing Machines, Inc. **62**

### Corrosion Inhibitor

CWT 118 is a nonchromate scale and corrosion inhibitor designed for use in open, recirculating, cooling water systems. The inhibitor is a stabilized blend of inorganic and antifouling agents and is particularly effective in the pH range of 7 to 8. It disperses mud, silt, process contaminants, and insoluble metal oxides and carbonates. Drew Chemical Corp. **63**

### Spectrometer-Chromatograph Aid

V-5500 MS/GC accessory transfers organic materials in gas chromatographic effluents from the GC flow stream to the source of a mass spectrometer, while simultaneously preventing any appreciable flow of carrier gas into the mass spectrometer. Based on the Llewellyn permeable barrier molecular separator, the accessory is useful in the continuous qualitative identification of the separated components of complex mixtures as they emerge from a gas chromatograph. Varian Associates. **64**

**$SO_2$ Monitor**

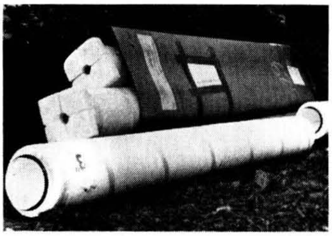
Model 11-7000 monitor is an electroconductivity analyzer for measuring atmospheric $SO_2$ concentration in two automatically-selected ranges (0 to 1 and 0 to 5 p.p.m.). The analyzer samples, analyzes, and continuously records $SO_2$ levels in air providing a measure of absolute concentration, not integrated value or periodic average. Davis Instruments. **65**

**Hydrocarbon Monitor**

Based on the principle that hydrocarbon molecules ionize in a hydrogen flame, Model 11-654 flame ionization meter measures atmospheric hydrocarbon concentrations in the 20 to 20,000 p.p.m. range. Methane is used to calibrate the instrument. A portable unit is available. Davis Instruments. **66**

**Dispersant**

Drewsperse 732, a liquid dispersant, retards the formation of precipitates in aqueous systems containing excess calcium, magnesium, iron, and copper. The material is useful as a water softener and prevents the deposition of iron oxide and red water conditions. Drew Chemical Corp. **67**

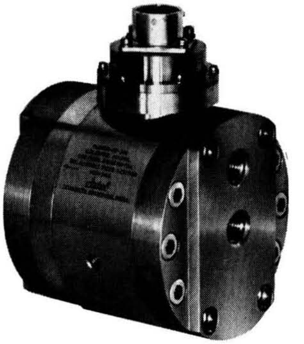


**Expandable Casing**

Bury-Pac, an expandable polystyrene casing, is useful for making Pyrex brand underground piping for acid waste removal permanent. Bury-Pac is available in five-foot half-section with inside diameters of 1½, 2, 3, 4, and 6 inches. Dow Chemical Co. **68**

**Gas Chromatograph Integrator**

An integration system for use with any gas chromatograph, the Kent Chromalog can be connected directly to a thermal conductivity detector or to the output terminals of any detector pre-amplifier. Input ranges of 0–½ mv. and 0–10 mv. are available in five discrete steps with a counting rate of 2500 c.p.m. at full scale on all ranges. The temperature coefficient of the integrator is less than 0.01 per degree C. Chemicon Co. **69**



**Pressure Transducer**

Model PL385TC is a corrosion-resistant, unidirectional, differential pressure transducer that measures pressure ranges of 0–5 and 0–50 p.s.i.d. Statham Instruments, Inc. **70**

**Turbidity Analyzer**

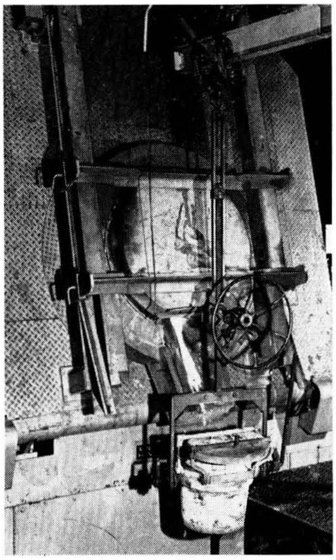
Operating on the principle of the Tyndall Effect, Model 370-A analyzer measures turbidity continuously in fluid flow up to 75 g.p.m. The analyzer handles fluids up to 450° F., and readout ranges of 0.001–1.0 p.p.m. and 1.0–500 p.p.m. are available. Gam Rad, Inc. **71**

**Liquid Scintillation Counting Vials**

Value Vials are available for measuring low levels of radioactivity, below 1 to 5 × background. Beckman Instruments, Inc. **72**

**Gas Chromatography**

Model 477 electronic digital integrator automatically detects peaks from 0 to 140 mv., corrects for baseline shifts, and provides unattended peak integration of five digits. Precision and reproducibility are better than 0.1%. Varian. **73**



**Electric Induction Furnace**

A line-frequency coreless electric induction furnace produces an improved grade of iron at reduced cost. The unit has a holding capacity of 5 tons and a melting rate of up to 2 tons /hr. Sola Basic Industries. **74**

**Ozonator**

Model CP or Model W ozonators for the treatment of exhaust odor problems of an organic nature are useful in reducing the odor of sulfides and mercaptans, skatoles and other amines, phenols, and other odoriferous organic compounds emitted from sewage treatment plants, rendering plants, fish processing plants, and chemical plants. Welsbach Corp. **75**

**Wire for Stainless Steel Welding**

Staincor wire, types 308L, 309L, 316L, and 347, is useful in welding stainless steel. Of a thin-wall tubular construction, the wire consists of a low-carbon steel sheath with alloy powders contained in the central core. The alloy powder core can be changed to meet specific customer requirements. Air Reduction Co., Inc. **76**

**Clean Cabinets**

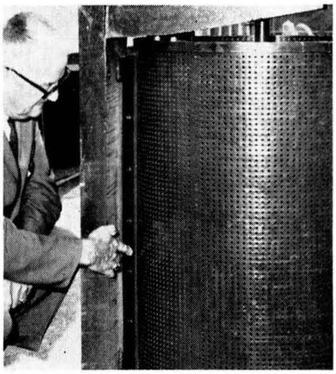
Three models of controlled-atmosphere cabinets for transporting, storage, or pass-through operations are available. These cabinets maintain dust-free, moisture-free (or inert gas) environments for microelectronic parts, subassemblies, miniaturized mechanical components, or biochemical mixtures. Air Control, Inc. **77**

**Clean Room Facilities**

Complete clean room facilities for precision cleaning, testing, assembling, and packaging of critically manufactured components are available on a contract basis. Design and construction of the clean room is based on the laminar flow principle. Michigan-Dynamics, Inc. **78**

**Coagulant**

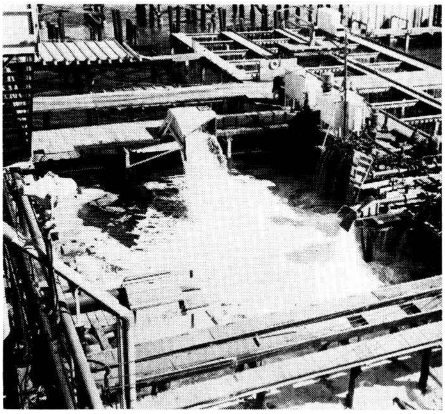
Nalcolyte 671 aids in clarifying industrial plant water for potable and general purposes, and for municipal water supplies, by increasing the size and settling rate of flocs formed by primary coagulants such as alum and iron salts. It also acts as a precipitation softening coagulant aid to increase size and settling rate of flocs formed by the primary coagulant (usually sodium aluminate) in softener-clarifiers. It is available in 50 pound, polyethylene-lined bags. Nalco Chemical Co. **79**



**Waste Water Heat Reclaimer**

Roto-Screen, a self-cleaning centrifugal screening device to prevent clogging in waste water suction pump lines, can be used to transfer heat from hot waste water to fresh water before the waste water is discharged to the sewage system. Patterson-Kelly Co., Inc. **80**

# NEW LITERATURE DIGEST



**Marine Corrosion**

*A revised edition of "Making the Ocean a Test Tube" describes continuing studies at the Habor Island Corrosion Laboratory near Wilmington, North Carolina for generating information on the effects of sea water, sea spray, and sea air on metals, woods, plastics, rope and plated and other surfaces. The 28-page booklet describes the selection of materials for applications involving exposure to marine corrosion and engineering applications such as hull materials, piping, heat exchangers, wire rope, decorative coatings, and the like. In the photograph a variety of test methods are used to study the corrosive effect of sea water flowing at high velocities. International Nickel Co., Inc.* **81**

**Pipe fittings.** Bulletin GS-101, *Compare*, lists the 10 most important characteristics of a pipe fitting, then compares the advantages and disadvantages of 5 different fittings types. Yarway Corp. **82**

**Condensate purification.** A 20-page report, technical reprint T-204, details the design, operational concepts, and comparative cost of the Powdex process for producing a high-quality feedwater. Graver Water Conditioning Co. **83**

**Scrubbers.** A 4-page illustrated catalog sets forth specifications for standard and special applications of two models of scrubbers for high-efficiency gas cleaning in foundry, cupola, rock drying, and chemical processing. Capacities and dimensions are listed. Buell Engineering Co. **84**

**pH meter.** A 4-page bulletin describes model 801 all-electronic digital pH meter for use with the company's series of specific ion electrodes. Orion Research Inc. **85**

**Rotameter.** Catalog 10A1000-67 is a 24-page buyer's guide for selecting, pricing, and ordering variable area flowmeters. The guide includes theory of operation, directions for sizing, and nomographs for both liquid and gas service. Fischer & Porter Co. **86**

**Instruments.** A 48-page condensed catalog (1966 edition) lists instruments for ASTM testing and biochemical instrumentation, and equipment for environmental and constant temperature control, materials evaluation, rubber testing, spectroscopic analysis, superpressure maintenance, and titration. American Instrument Co., Inc. **87**

**Spectrum scanner.** Volume 22, No. 2 of *Spectrum Scanner*, a bimonthly publication describing instruments and applications in the field of emission spectroscopy, atomic absorption spectroscopy, the physical sciences, and x-ray diffraction, is available. Jarrell-Ash Co. **88**

**Investment opportunities.** A 4-page leaflet proposes that the pollution field is a good opportunity for investment, lists specific stocks to buy. Paine, Webber, Jackson, & Curtis (Members New York Stock Exchange). **89**

**Air heaters.** The mixing of combustion gases and process air in direct-fired air heaters for spray dryers, rotary dryers, tunnel dryers, ovens, and kilns is described in bulletin 130. A heater selection guide is included. Thermal Research & Engineering Corp. **90**

**Pumps and water systems.** An 8-page booklet shows a line of pumps to meet the needs of homeowners, builders, small industry, and farms. Pumps shown include jet pumps for shallow or deep well installation, two models of submersible pumps, sump pumps and drainers, and engine-driven self-priming pumps. Colt Industries. **91**

**Environmental simulation equipment.** Catalog 565 describes relative humidity- and temperature-controlled enclosures, subzero constant-temperature cabinets, high-temperature ovens, and constant-temperature baths. American Instrument Co., Inc. **92**

**Waste treatment process.** A new waste treatment process utilizes coagulants, coagulant aids, and settling time to effect clarification, followed by contact with granular activated carbon to effect simultaneous filtration of suspended solids and adsorption of dissolved organic contaminants. The company states that the new process is more efficient than bacteriological processes. Calgon Corp. **93**

**Steel drum opener.** A motorized unit able to dehead a 55-gallon steel drum in two minutes is illustrated in a 4-page folder. The process is faster than other methods, more economical since emptying is more efficient, and leaves a smoother edge, says the company. Hydro-Thermal Corp. **94**

**Electronic balance.** A 4-page bulletin gives design and performance data for an electronic analytical balance featuring full digital readout. Two special models are described: one for air pollution filter sheet weighing or for weighing large or bulky items, the other for remote operation when materials are weighed in special environments or within protective enclosures. Torsion Balance Co. **95**

**Dust collectors.** Bulletin 925 gives information on the construction, operation, and application of dust collectors to the chemical industry. Pangborn Corp. **96**

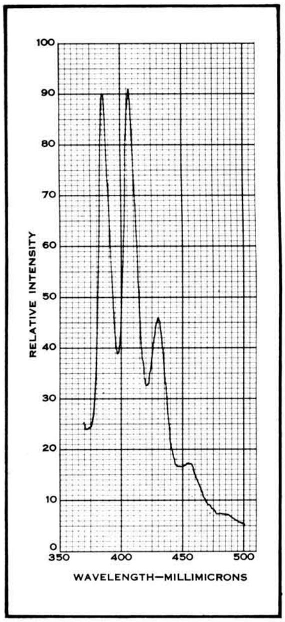
**Equipment catalog.** Catalog 67 contains 381 pages of scientific glassware and apparatus. Ace Glass Inc. **97**

**Flow rate indicator.** This 4-page folder describes a direct-reading, variable area impact tube flow rate indicator designed to measure flow of clean water. The liquid main stream does not pass through the meter, so there is no pressure drop involved in operation. Fischer & Porter Co. **98**

**Chemical catalog.** *Chemical Index 67-C* is a listing of more than 7000 inorganic and organic chemicals arranged in a three-section color-coded format for convenience. Fisher Scientific Co. **99**

**Pollution control programs.** Turn-key installations for air/water pollution control are described in this 10-page brochure. Erection, engineering and start-up, solvent and vapor recovery, custom distillation and chemical reaction services, and custom conversion of chemical byproducts to saleable end products, are covered. Mercury Chemical Corp. **100**

**Public affairs pamphlet.** The cause and sources of air pollution, its cost in terms of human discomfort, disease, and economic waste, and what can be done about it are outlined in *The Battle for Clean Air*, by Edward Edelson. This new pamphlet is available for 25 cents from the Public Affairs Committee, 381 Park Avenue South, New York, N.Y. 10016. Public Affairs Committee, Inc. **101**



# MEETING GUIDE

**October 3–5**
**Association of Analytical Chemists**

1967 Anachem Conference

Statler Hilton Hotel, Detroit, Mich.

The conference will feature eleven symposiums, an exhibit of new instruments, and the presentation of the Anachem Award to an outstanding analytical chemist. Symposiums will be devoted to particle size analysis and environmental analysis from air pollution, biochemical phases, and water pollution.

**October 4**
**Air Pollution Control Assoc. (Mid-Atlantic States Section)**

Semi-Annual Technical Conference

Penn-Harris Hotel, Harrisburg, Penna.

The theme of the one-day conference will be "The Economics of Air Pollution." The meeting will feature a luncheon address by Governor Raymond P. Shafer (Pa.); a paper entitled "The Economic Aspects of Air Polluton as Seen by the Federal Government" by Dr. J. T. Middleton of the NCAPC; among others.

**October 8–12**
**Institute of Sanitation Management**

Annual Environmental Management Conference and Maintenance Exposition

Mayflower Hotel, Washington, D. C.

Designed to assemble the leading environmental sanitation executives and managers from throughout the U. S., Canada, and many foreign lands, the conference will feature as its general theme, "Environmental Sanitation is Shaping Tomorrow."

The four-day conference will feature education and technical sessions, round table discussions, problem solving clinics, and the annual Sanitation Film Festival. The three-day exposition (Oct. 8–10) will feature the latest equipment, supplies, and services available within the environmental sanitation maintenance field.

**October 10–11**
**Industrial Hygiene Foundation**

32nd Annual Meeting

Chatham Center, Pittsburgh, Penna.

Scientific, health, and industrial advancements in environmental health will be discussed by internationally known leaders. The meeting will feature sessions on management, engineering, legal aspects, medicine and nursing, and chemical toxicology.

**October 16–20**
**American Society of Civil Engineers**

Water Resources Engineering

Statler Hilton Hotel, New York, N.Y.

Water resources planning, urban planning, water power and service continuity, flood damage reduction, pipeline design, tidal hydraulics, water regulation and rights, river and lake control, and weather modification will be discussed during the first three days of the meeting. Low flow hydrology, dams, drought, ground water, eutrophication, and watershed management are among the topics to be presented during the final two days.

**October 19–20**
**Clemson University-Department of Chemical Engineering**

Seminar on Air and Water Pollution Control

Clemson University, Clemson, S. C.

Technical sessions will be presented on present laws, instrumentation, process monitoring and control. The second seminar is jointly sponsored by Clemson University, the American Institute of Plant Engineers, and the South Carolina Pollution Control Authority.

**October 23–24**
**Metropolitan Engineers Council on Air Resources (MECAR)**

New Developments in Air Pollution Control

Commodore Hotel, New York, N.Y.

The two-day technical symposium will emphasize major developments in the areas of recovery of sulfur oxides from stack gases, control of noxious gaseous emissions, control of particulate emissions, and control of solvent emissions. Attendance is limited and will be by preregistration only, $15.00 per person. Contact Robert A. Fox, P.O. Box 607, Grand Central Post Office, New York, N.Y. 10017.

**October 23–24**
**1967 Cleaner Air Exposition**

Commodore Hotel, New York, N.Y.

The exposition is held in conjunction with the nationwide observance of Cleaner Air Week, October 22–28. It will feature exhibits by manufacturers of air pollution control equipment, publishers of air pollution control literature, consulting and engineering services, and air pollution control agencies.

**October 23–27**
**American Public Health Association**

95th Annual Meeting

Fontainebleau Hotel, Miami Beach, Fla.

A special session on environmental health will cover man-made environmental hazards and what can be done to restore the environment. Another featured session will be on the maximum social use of land, air, and water resources. Other topics include respiratory diseases in industry, use and control of radiation in clinical medicine, health problems in the aerospace industry, noise and its impact on health, laboratory analytical methods in environmental surveillance, environmental epidemiology, and comprehensive environmental health planning.

**November 6–7**
**Oklahoma State University**

18th Oklahoma Industrial Wastes and Pollution Control Conference

Oklahoma State University, Stillwater

The four half-day sessions in this special two-day technical seminar will be on the subjects of solids control, use of activated carbon for treatment of organic wastes, inorganic treatment, and reverse osmosis treatment.

**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 radioisotope techniques in ground water resources investigations.

## MEETING GUIDE continued

**November 8–10**
**American Water Resources Association**

3rd Annual American Water Resources Conference

Mark Hopkins Hotel, San Francisco, Calif.

Planned to follow the National Symposium on Ground Water Hydrology, the conference will comprise sessions on water resources planning, pollution control, and computer applications on water resources engineering, among others.

**November 10**
**Association for Computing Machinery**

Annual Symposium on The Application of Computers to the Problems of Urban Society

Hilton Hotel, New York, N.Y.

The one-day symposium will feature sessions on air and water pollution, urban planning, and others.

**November 13–15**
**University of Delaware**

1st Annual Mid-Atlantic Industrial Waste Conference

University of Delaware, Newark, Del.

Air and water pollution abatement measures for industry—both chemical and agricultural—will be discussed.

**November 20–22**
**Saul Gordon Associates**

Workshop on Noise—Its Measurement and Control

Hopatcong, New Jersey.

A three-day workshop will provide attendees with an introduction to the theory and instrumentation needed for noise measurement and control, and will emphasize common measurements and analysis pitfalls. Both lecture and laboratory sessions are planned. Noise measuring equipment of various manufacturers will be demonstrated. Tuition for the workshop is $120. Lodging fees are $48 for resident participants and $30 for non-resident participants.

**November 26–30**
**American Institute of Chemical Engineers**

60th Annual Meeting

Hilton Hotel, New York, N.Y.

Among the 42 symposiums scheduled for this meeting are symposiums on the developing technology for water pollution abatement (Nov. 30) and the effects of government regulations on processes for air pollution abatement (Nov. 29).

**November 27–30**
**Entomological Society of America**

1967 Annual Meeting

Hotel New Yorker, New York, N.Y.

The implications of insecticide choice, and pesticide movement and degradation in soils, among other topics, will be discussed.

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## MEETING GUIDE continued

**November 27–December 1**
**International Exposition Company**

31st Exposition of Chemical Industries
Coliseum, New York, N.Y.

Of the more than 550 exhibits enrolled for display, the Exposition will feature equipment for air and water pollution control, dust and fume collection, and water treatment including the latest methods of waste disposal. Advanced instrumentation for monitoring air pollution and water pollution and water purity will be included in a display of on-stream equipment for industrial applications. A recording bolometer will be offered to monitor air pollution. This instrument measures contamination of air in terms of the radiant energy of floating particles.

**December 4–8, 1967; January 22–26, 1968; April 1–5, 1968; April 15–19, 1968; May 27–31, 1968**
**Manufacturing Chemists Association**

Seminars on Water Pollution Control for Chemical Wastes
University of Texas, Austin

Each seminar is designed as an intensive course on chemical waste treatment for water pollution control. Under the direction of W. Wesley Eckenfelder, Director, Program for Advanced Study in Water Pollution Control, these seminars will provide attendees with the latest techniques in the field both as to practice and as to the selection, planning and designing of particular treatment methods. Registration is available to industrial representatives only and should be made to the MCA. Fee for each seminar is $150 and the schedule is;

- December 4–8, 1967
  - Vanderbilt University
  - Nashville, Tennessee
- January 22–26, 1968
  - University of California
  - Berkeley
- April 1–5, 1968
  - University of Illinois
  - Urbana
- April 15–19, 1968
  - Manhattan College
  - New York City
- May 27–31, 1968
  - University of Waterloo
  - Ontario, Canada

**March 31–April 5, 1968**
**American Chemical Society-155th National Meeting**

Symposium on Developments in Petroleum Environmental Chemistry
San Francisco, Calif.

Jointly sponsored by the Divisions of Petroleum Chemistry and Water, Air and Waste Chemistry, the theme of the symposium will include the chemical characterization and chemical control of aqueous and gaseous wastes from the production, refining, distribution, and use of petroleum products. Members only of the ACS wishing to present papers should submit titles and abstracts no later than Nov. 1, 1967 and complete papers no later than Nov. 15, 1967 to either the chairman, Mr. J. Cohen, FWPCA-USDI, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio 45226 or the cochairman, Dr. C. E. Moser, Texaco, Inc., Beacon, N. Y. 12508.

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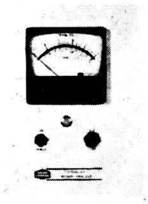
# When you are running as many chemical plants as Union Carbide, you want the best dissolved oxygen analyzer you can buy.

That is why we decided to build our own.

Now you can own it for just $800.



The Union Carbide Model 1101 Dissolved Oxygen Analyzer was built to meet a very real need. In our own plants.

We wanted accurate readings for months at a time without maintenance, without clogging or fouling by oil, sediment, or biological growth. *We have it.* (One major city has been using this DOA without touching the probe for six months!)

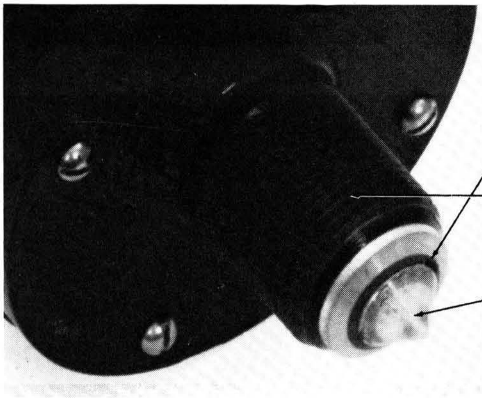
We wanted fast . . . very fast . . . response to changes in dissolved oxygen levels. To give us complete and accurate control of boiler feed and condensate, process water, effluent, or sewage treatment. We have response down to a few seconds, continuously.

We also wanted some special features: A reference electrode with no external electrolyte reservoir. DO readings automatically compensated for temperatures between 0 and 50 deg. C. and instantaneous temperature readings with a flick of a switch. A linear output displayed on a meter, chart, recorder, or at remote locations. Plus the rugged, long life construction that can only come with printed circuits and solid state electronics.

*What is the secret* behind all of these innovations? The heart of our system lies in the tip of our probe. Here we have combined a thallium electrode, a reference electrode and a temperature sensor in an exclusive measuring cell. In fact, U. S. Patent No. 3,218,242 makes sure it is exclusive.

There is a lot more information about the 1101 DOA in our 12 page booklet. Write for it by using the coupon below. And ask for data on our other environmental instruments as they go into production.

When you have 380 mines, mills, labs and plants around the world, you build the instruments you can't buy.



**Oxygen concentration** in water stream is measured by the reaction between thallium electrode and dissolved oxygen. Cell e.m.f. rises as oxygen concentration increases.

**Temperature sensor** in probe compensates cell for temperature changes (0-50°C) and provides temperature indication.

**Self-cleaning,** non-destructive design of probe permits months of operation without attention. No membranes to clean or replace. Rugged enough to stick in a river.

Please send me the 12 page booklet on the *Union Carbide* Dissolved Oxygen Analyzer. My application is for measuring dissolved oxygen in:

____________________

Name____________________

Title____________________

Company____________________

Address____________________

City____________________

State__________ Zip________

*Mail to:* Union Carbide Corporation,
Instrument Dept., 5AY New Street,
White Plains, N.Y. 10601

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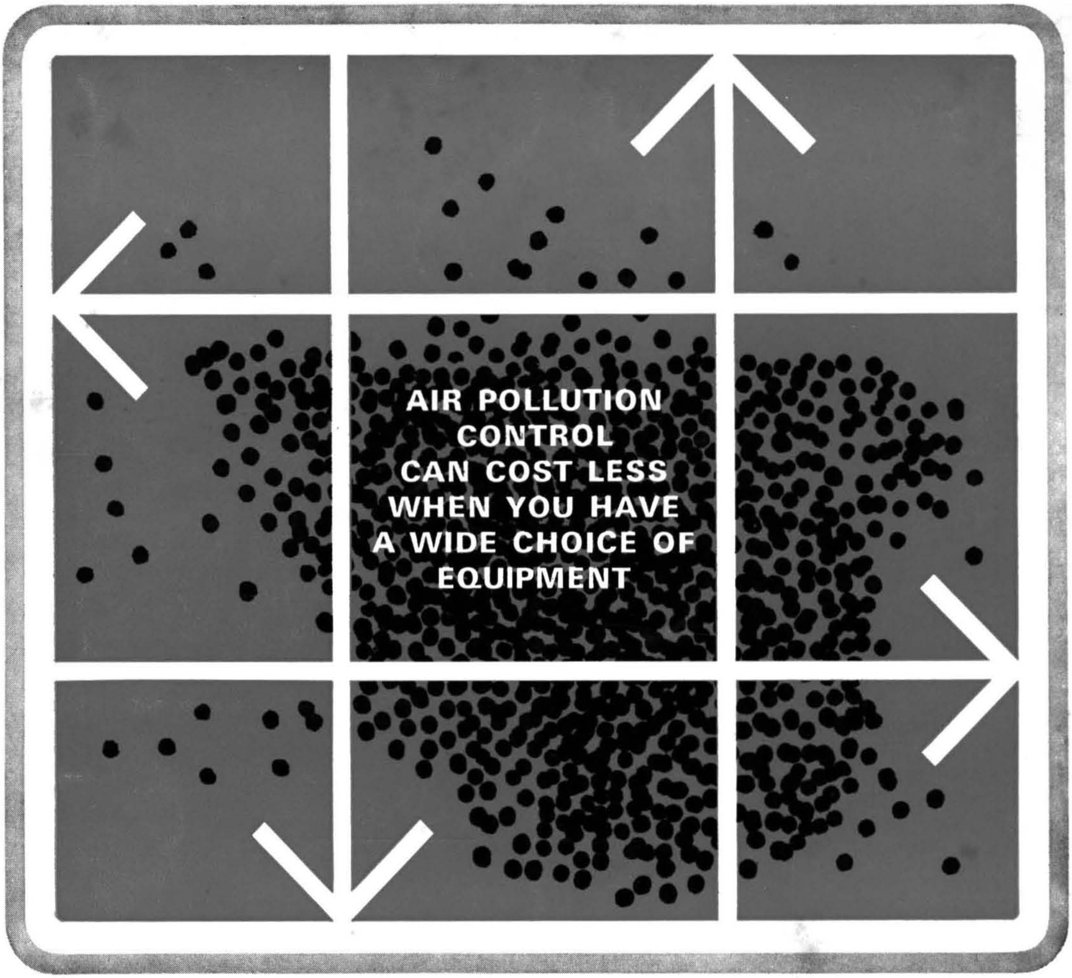
UNION CARBIDE INSTRUMENTS

Visit our exhibit at the WPCF Meeting in New York, Americana Hotel, October 8-13.



There are probably at least two solutions to your specific air pollution problem—each one capable of doing the clean-up job you require.

If the pollutant is a gas, for example, you may have a choice between wet scrubbing, catalytic or thermal incineration and carbon absorption. If it's a dust problem, for example, you may have a choice between centrifugal collection, precipitation, filtration and wet scrubbing.

### *But which one will cost you less?*

UOP can give you an objective answer, because we offer all four types of equipment for gases (plus others for particulate collection). And economic analysis is just as important a part of our proposal studies as technical feasibility.

Ask UOP to quote—you may be surprised at the savings you get. And write for UOP Air Correction literature. UOP Air Correction Division, Universal Oil Products Company, Greenwich, Connecticut 06830.

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