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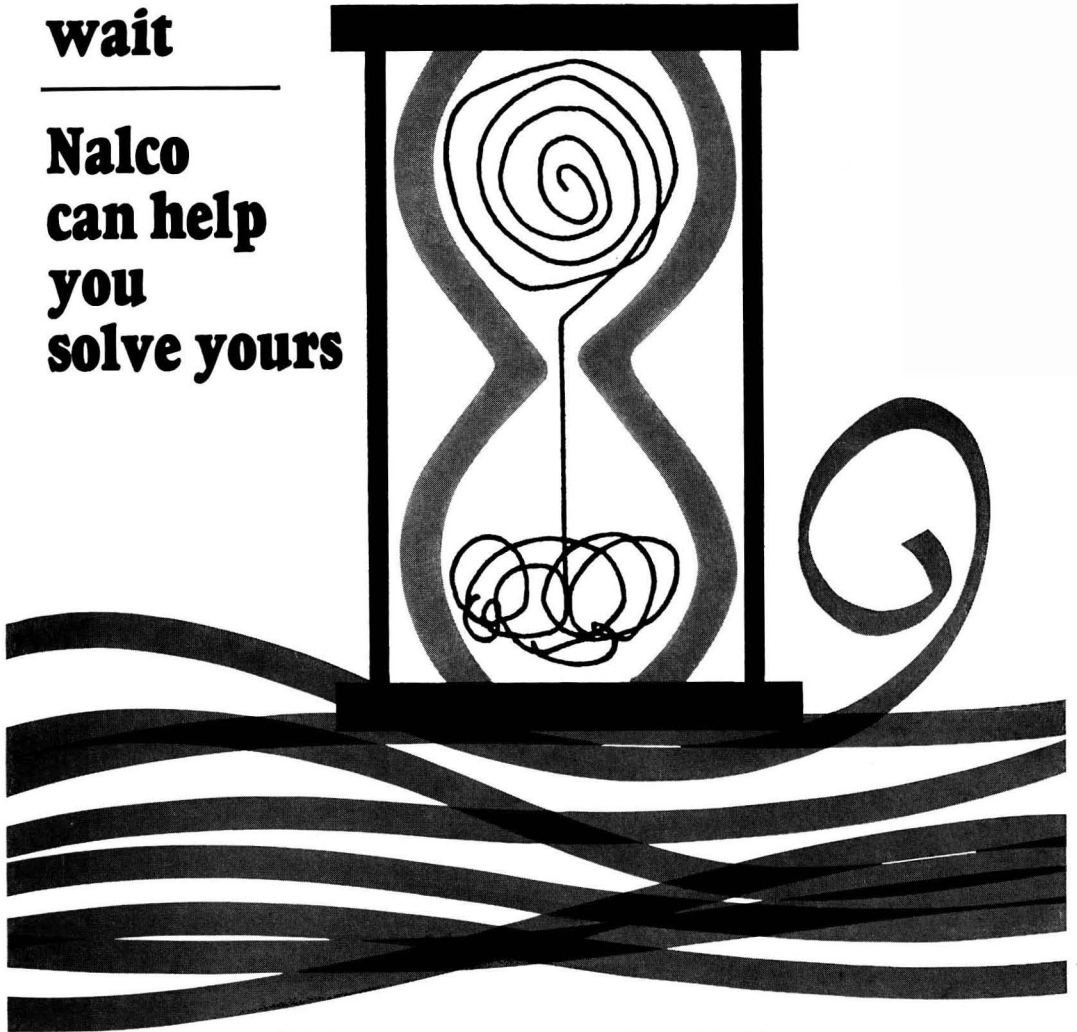
Pollution Control Services represents the combined knowledge and experience of all Nalco divisions—mobilized for action! This coordinated force can help you find a practical solution, regardless of what your industrial or municipal pollution problem may be. This includes control of the whole ball of waste, from raw water intake through manufacturing processes to the final effluent. It's simpler that way. And faster. For details, contact your local Nalco field representative, or write Nalco headquarters in Chicago for our "Management Guide to Pollution Control."

Nalco **POLLUTION CONTROL SERVICES**

Nalco Chemical Company, 180 North Michigan Avenue, Chicago, Illinois 60601

ENVIRONMENTAL
Science & Technology

CONTENTS

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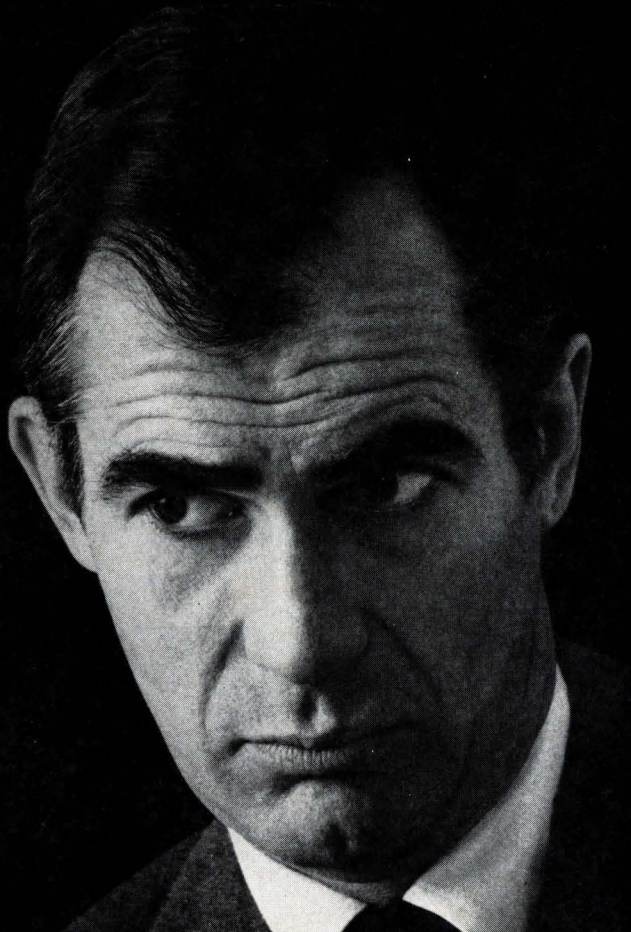
Congress Told about Positive Face of Health

Disease prevention is only part of the air pollution control story, contended Dr. William H. Stewart, Surgeon General of the U.S., in his testimony last month before the Senate Subcommittee on Air and Water Pollution. He stated that it is now possible, because of advances in medical science, to think about "the positive face of health—the quality of individual living." Prevention of odor and unpleasant effects which do not necessarily cause disease should also be a goal of pollution control legislation, Dr. Stewart added. He was followed by Dr. John Middleton, director of the National Center for Air Pollution Control, who noted that the public no longer seems willing to grant its lawmakers and public officials the right to do nothing about an area's air pollution problems (ES&T, March, page 206). He then testified that air quality criteria for several important pollutants would be ready for publication before the end of 1967 (see page 282). Also from NCAPC were Mr. S. Smith Griswold—pollution abatement, control development, and training activities; Dr. Edward T. Blomquist—procedure for establishing criteria and standards; and Dr. John H. Ludwig—development of technology for controlling air pollution.

MCA on Tax Credits

The Manufacturing Chemists Association is objecting to the proposed regulations on certification of air pollution control facilities for investment tax credit purposes. MCA objects on two main counts. First, it objects to the proposal that the state first approve the facilities. In a letter to the Department of Health, Education, and Welfare, executive secretary Maurice F. Crass, Jr., says that the state agency and HEW should consider applications independently and simultaneously. Also, the letter says that HEW should "look only to federal law and requirements which have been promulgated as regulations applicable to the facility for which certification is requested" and not on guides for good practice or other criteria which do not have the force of law.

Lake Michigan Cleanup

Most of the chemical, petroleum, and other industrial plants around the southern tip of Lake Michigan are either already doing a satisfactory water control job or are on schedule with clean-up plans. But the biggest polluters —U.S. Steel, Inland, and Youngstown—are two years behind the schedule which calls for complete cleanup by 1968. This was the thrust of testimony given at the recent one-day conference in Chicago called by the Federal Water Pollution Control Administration to check progress in the two-year battle to stem severe pollution in that area. Unmoved by pleas from the steel companies for an extension, the conferees unanimously agreed to maintain the 1968 deadline. At their next meeting in September, however, they could extend the deadline. They also have the power to take laggard companies into court. Despite the progress, the overall program has had little effect on water quality in the area.

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Instrumentation for Clean Water Standards

States will have the instrumentation needed to enforce the clean water standards they must enact by June 30, said Honeywell Industrial division's senior application engineer, J. B. Stickley, in Minneapolis at a meeting last month of the Minnesota Association of Consulting Engineers. But, says the Honeywell engineer, in one key area—that of sensors for measuring pollutants—"the state of the art leaves much to be desired." Of the more than 45 variables so far identified, only about 15 are measurable on a continuous or reliable basis. "The remainder are measurable only under laboratory conditions or with automated wet chemistry techniques, if at all," he concluded.

The Torrey Canyon Affair—A Bit Airy Fairy

Although the initial ecological effects of the *Torrey Canyon* episode are apparently relatively minor, the situation is, "a bit airy fairy," says a British official. All the consequences of the disaster may not be known for years. According to Home Secretary Roy Jenkins, fish in the Seven Stones reef, where the supertanker ran aground March 18, were, several weeks later, untainted and seemed plentiful as ever. "Close in shore," he added, "where shellfish might be affected, only very few crabs and shore-haunting fish have been found dead. This was in areas heavily polluted with oil and where substantial quantities of detergent have been used. This is being kept under review by experts reporting to the government's chief scientific adviser, and local authorities have been asked to restrict such detergent operations wherever feasible." (About 1 million gallons of 12 different detergents, much of which was a kerosine extract with emulsifier added supplied by British Petroleum, were sprayed on the oil slicks.) Among wild birds, there have been "a lot of casualties," one British observatory estimating that 40,000 seabirds died.

Despite all attempts at preventing the oil from getting to the coasts, close to 80,000 of the 117,000 tons of the Kuwait crude carried by the *Torrey Canyon* fouled, or threatened to foul, the British and French coasts. The beaches are now being cleared up, but a potential problem still remains: some of the oil, both untreated and emulsified, has penetrated the sand deeply and might be brought up again by tidal action. Permanence of effects of both oil and detergent on animals and plants is as yet unknown. But some idea of the magnitude of the problem comes from Clive Manwell of the Marine Biological Association in Plymouth, who describes an eight-year study of the ecological effects along a beach severely damaged in 1957 by 2000 tons of oil from a vessel run aground off Baja, Calif. No detergent was used. There was still "considerable instability, even below the tide line," after eight years. In the laboratory, he says, the detergent being used causes more harm than the crude oil.

The *Torrey Canyon* episode is by no means unique—what is unprecedented is the quantity of oil involved. Last month beaches along the east coast of the U.S., especially off Boston, were being threatened with a major oil pollution problem. Although the source has not been pinpointed, evidence points to an oil tanker torpedoed during World War II.
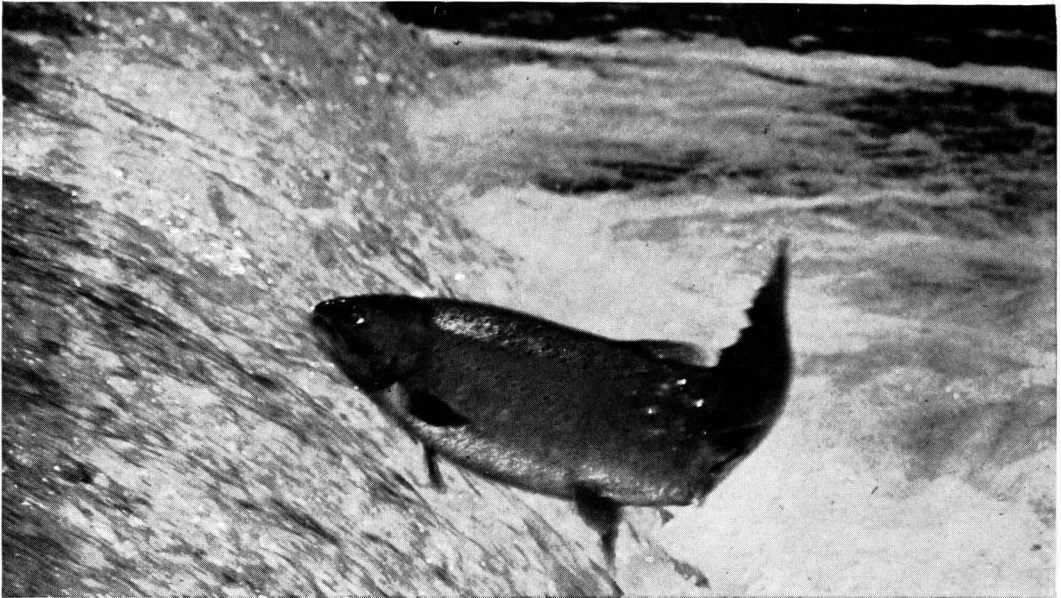
PHOTO BY ROY HIDER

Foxboro helps Kimberly-Clark keep a river <u>alive</u>

Even spawning trout and salmon in the Sacramento River don't know they're swimming in used water. So clean is the discharge from the new Kimberly-Clark paper mill at Anderson, California, that nearly 11-million gallons a day flow downstream without disturbing the river's natural balance. As a result, Kimberly-Clark has been commended by the Secretary of the Interior for their accomplishments.

Many other leading companies throughout the process industries have joined the fight against air and water pollution. In many of these installations, Foxboro instruments are helping them make dramatic progress.

Whatever your company's pollution problems, you'll find Foxboro engineers can help you get the most out of your investment in pollution abatement. For information on this specialized Foxboro capability, write for Bulletin B-16. The Foxboro Company, 754 Norfolk Street, Foxboro, Massachusetts 02035.
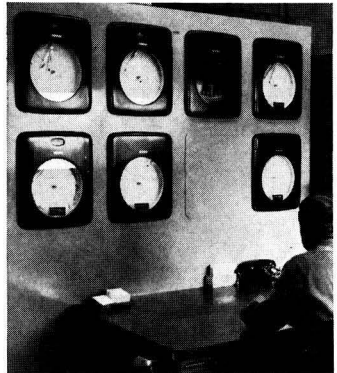
Dependable Foxboro instrumentation is used in Kimberly-Clark's modern waste treatment system to control flows and record other vital process information.

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Reducing Emissions

A number of major industries may be subject to uniform emission control standards if presently proposed legislation is adopted. Dr. John T. Middleton, director of the National Center for Air Pollution, lists the industries as: power, ferrous metals, nonferrous metals, coking, petroleum, pulp and paper, cement and lime, sulfuric acid, nitric acid, phosphate fertilizer, glass (including glass fiber), and other chemicals (including detergents).

Better control of combustion is one promising approach to reducing emissions. Work at the Bureau of Mines' Explosives Research Center is focusing on how flames produce carbon monoxide and nitrogen oxides from carbon in fuel and nitrogen in the air. Experiments with propane gas flame show that when combustion gases are cooled rapidly, less nitric oxide is formed. The bureau plans similar studies with other fuels to throw light on the origin of nitrogen oxide in auto exhaust. The flames are also being studied in an attempt to identify the factors governing the presence of residual hydrocarbon compounds in automotive exhaust gases.

Improved design of incinerators is another way of cutting down emissions into the air. BuMines has designed experimental incinerators based on the tangential overfiring principle. The major problem in burning refuse is poor air distribution. Instead of supplying air from below a grate, BuMines supplies it from above. The air swirls in at an angle, spiraling down the walls of a cylindrical combustion chamber toward the refuse bed. BuMines cites these advantages of the technique: Combustion is more complete since airflow can be controlled better and since refuse particles rising through the chamber in the exhaust gases (also flowing in a spiral pattern) have more time to burn completely. Also, air swirling down the hot inner walls is preheated, promoting greater thermal efficiency. BuMines got virtually complete destruction of wastes with emission of clean exhaust gas in tests with three small incinerators.

Incinerator design got another assist, this time from equipment long familiar to power plants, steel mills, and chemical plants. The City of Montreal has ordered an electrostatic precipitator for its new steam-generating incinerator. Research-Cottrell, Inc., the supplier, says that this is the first such use in North America. Ash emissions will be less than 0.2 pound of particles per thousand pounds of gas (corrected for 50% excess air), about half that of the best of latest designs, says Research-Cottrell. Despite the initial cost of the equipment, Montreal expects to make $500,000 annually by selling the steam generated at the plant. Research-Cottrell says it can provide precipitators for existing as well as new incinerators, but it does not recommend them for incinerators of less capacity than 50 tons per day, nor those used only intermittently. Research-Cottrell also disclosed it has installed two flooded disk scrubbers at Atlanta Scrap Processors, Inc.'s new kiln for making scrap from auto bodies. Sheared cubes of auto body scrap enter the kiln, where combustibles burn out and glass and nonferrous metals melt and are separated after quenching. The stack gas is clean enough to permit locating such plants near urban areas, a crucial point in avoiding the excessive hauling costs that make such operations uneconomic, says Research-Cottrell.

OUTLOOK

Demands for Better Water
Boost Water Chemical Market

**Charles H. Kline and
Thomas S. Bry**

*Charles H. Kline & Co., Inc.
Fairfield, N. J. 07006*

Our growing requirements for water, often of higher and higher quality, and the public demand for greater control of pollution are creating substantial markets for chemicals. U.S. industry and local governments spent about $250 million for chemicals for water management in 1966. This sum may nearly triple in the next 10 years.

When most people consider water treatment, they think first of the familiar municipal waterworks and the chlorine, alum, lime, soda ash, and other heavy chemicals it consumes. Such a view is far too limited. Actually, the municipal segment represents only about 20% of the total market for chemicals in water management. Also, this segment has the lowest rate of growth in the whole field. Finally, the major opportunities for chemical companies to profit from the growing field of water and waste treatment lie not in the low cost heavy chemicals but in higher priced specialty products sold either in bulk or as formulated products.

By far the largest segment of the U.S. market for chemicals in the water treatment and pollution control is internal treatment of industrial water

Water management cycle is complex and takes a variety of chemicals

Well

Lake or reservoir

Biocides

River

Bulk supply water treatment plant, municipal and industrial

Supply water treatment chemicals
Adsorbents and oxidants
Acids and bases
Coagulants
Disinfectants
Filter media
Fluorides
Iron and manganese removers
Sludge conditioners
Softeners

Town: Residential section

Electric utility
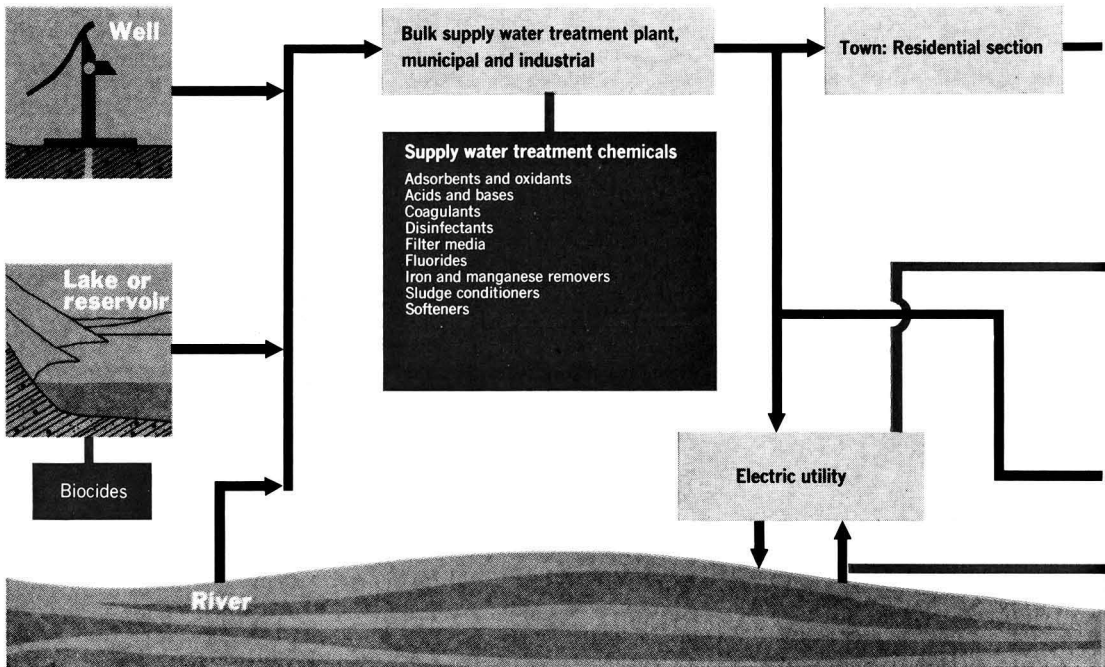
*Bulk of chemical sales to water treatment and pollution
control market is for internal treatment of industrial water.
Chemicals for pollution control account for only 10% of the total market*

at the point of use for boilers, cooling systems, microorganism control, and process applications. Treatment of bulk supply water for municipalities and industry is the next largest segment. Surprisingly, pollution control today accounts for only about 10% of the total market.

Internal treatment

Internal treatment of industrial water is a highly sophisticated art. For example, drinking water of good quality may carry up to 500 p.p.m. of dissolved salts; and in some communities drink-

ing water carries over 2000 p.p.m. of salts. Indeed, drinking water with no dissolved salts tastes flat. On the other hand, the allowable total salts content in a modern steam power plant designed for ultrahigh pressure is measured in parts per billion.

Chemicals sold for internal treatment of water are generally formulated products, often containing several different chemical compounds. The total number of products is immense; the leading companies each offer several thousand individual formulations. However, the business is concentrated in a

few principal types of applications. A very rough breakdown of present annual sales by principal application is shown in the following table:

Application	Millions of dollars
Boiler feed and condensate	$ 60
Cooling towers and systems	40
Other microorganism control	20
Process water and other	30
Total	$150

In **boilers** the principal problems of internal water treatment are the prevention of the following:

• Scale, especially on the water side.

Internal treatment chemicals

Boiler water
Cleaners
Corrosion inhibitors
Demineralizers
Foam controllers
Scale controllers and polymers

Cooling and process water
Biocides
Corrosion inhibitors
Demineralizers
Scale controllers
Wood preservatives

Waste treatment chemicals

Adsorbents
Acids and bases
Biological nutrients
Coagulants and polymeric
  acids
Disinfectants
Filter media
Foam controller
Special oxidants
Sludge conditioners

Municipal sewage plant

River, lake, or ocean

Town: Industrial section

Once-through cooling; chlorine

Industrial waste plant

Ponds   Lagoons

Annual sales of chemicals for water treatment and pollution control reach $250 million

All figures in millions of dollars

Municipal $10 million
Pollution control $25 million

Industrial $15 million

Industrial $20 million

Internal treatment $150 million

Bulk supply water treatment (external) $75 million

Municipal $55 million
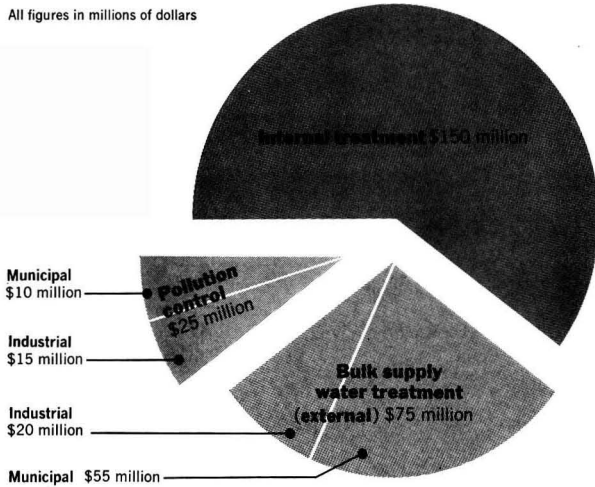
Sales of chemicals for water management are now $250 million annually. The familiar municipal waterworks account for only one fifth of the total market. Industrial water treatment, particularly for boilers, cooling towers, and process use, takes the largest part, by far. Sales of chemicals for pollution control are relatively low, but are growing rapidly

• Corrosion, particularly on the vapor side.
• Carry-over of solids and moisture.
• Caustic embrittlement.

In high pressure steam turbines, carry-over of silica is particularly troublesome. Silica volatilizes above 600° F. and is carried over to the turbine blades. Silica contents above 20 p.p.b. form deposits on the blades and thus lower the efficiency of power generation. Accordingly, most large power installations demineralize both makeup water and condensate return and continuously monitor the system for silica content.

In **cooling water,** chemical treatment is particularly important in open recirculating systems employing cooling towers. Major problems in such systems are the prevention of the following:

• Fouling by microorganisms.
• Destruction of the tower lumber.
• Corrosion.
• Scale.

Once-through cooling water and closed recirculating systems are also treated, but they account for a considerably smaller market.

Microorganism control is important in many industrial operations other than cooling towers. Among major markets

are paper mills, oil-well drilling, and water-flooding operations. Because all these locations offer near-ideal conditions for growth of slime, fungi, and bacteria, regular treatment with an effective biocide is essential.

Water also requires treatment for a great variety of such process uses as the production of chemicals, drugs, cosmetics, beverages, and electronic products. For example, particularly stringent requirements are placed on the treatment of water used in the manufacture of phosphors for color television screens and other electronic components.

Indirect selling

Few manufacturers of the basic chemicals used in formulated products for various applications sell much direct to the end user. In general, a specialized group of water-treatment companies buys the basic chemicals, formulates them into end products, and sells these end products—together with a very considerable amount of service— to the industrial plants or operations that are the ultimate consumers. Some large utilities purchase basic chemicals direct from the manufacturer. However, most industrial plants find it more convenient to retain one of the water-

treatment companies to diagnose their problems, recommend suitable treatment, and supply the necessary formulated products.

In all, there are several hundred of these companies throughout the country. Most of them are small and serve only a local area or a particular industry; only about 10 companies market on a national or regional scale.

In their orientation toward formulation and service, these companies differ considerably from the traditional manufacturer of basic chemicals. For example, the water-treatment companies all have extensive sales staffs in the field. Nalco Chemical has 300 salesmen and Betz, 150. Calgon's Hall Laboratories Division consults for 2500 plants.

Some of the other differences between water-treatment and conventional chemical companies are revealed in a comparison of financial data for two publicly held water-treatment companies and a group of chemical manufacturers. Let us consider Betz Laboratories, a company almost entirely engaged in formulation and service, and Calgon, a company with extensive formulation and service activities, but also heavily involved in basic manufacturing, and compare them with an average taken for 30 large chemical companies, ranging from Du Pont with annual sales of $3.0 billion in 1965 to Emery Industries with annual sales of $45 million.

The two water-treatment companies (Betz and Calgon) have lower manufacturing costs as a percentage of sales than the chemical companies, partly because of their lower requirements for fixed capital. At Betz, one dollar of net worth (stockholder's equity) produces $3.10 of sales, as against $1.80 for a more traditional chemical company. Similarly, one dollar invested in land, buildings, and equipment (at first cost) gives $9.20 of sales at Betz, but only $1.30 at the average chemical company. Offsetting their low capital cost, the water-treatment companies have large sales and service costs. Selling, general, and administrative expenses are 36.0% of sales at Betz, as against 16.7% at the average chemical companies. However, this burden is not too severe; Betz had a return on net worth of 23.2% in 1965 and Calgon 18.4%, well above the chemical industry average of 13.0%.

As the water-treating companies grow,

and as specialty chemicals come to play an increasingly important role in their products, the larger formulation and service companies more and more are undertaking the manufacture of selected basic chemicals. For example, Nalco and Calgon both manufacture synthetic organic polymers for such uses as coagulant aids. Calgon recently acquired Pittsburgh Activated Carbon Co., the largest U.S. producer of granulated activated carbon. Betz makes a number of specialty organic chemicals and carries on an active program of synthesis of new products.

A number of the other water-treatment companies have manufacturing affiliates. Dearborn was recently acquired by W. R. Grace. Permutit is part of Ritter-Pfaudler, which has Ionac Chemical as a subsidiary. Nalco, Drew, and others manufacture a wide variety of basic chemicals.

For traditional chemical companies, internal water treatment represents a growing market for specialty products, for example the following:

Product	Function
Ion exchange resins	Demineralization
Natural and synthetic polyelectrolytes	Scale control and sludge conditioning
Hydrazine	Oxygen scavenger
Biocides	Slime, algae, and fungi control
Amines	Corrosion control
Specialty phosphates	Scale control

Some of these chemicals already have substantial sales volumes and the number will increase as the overall market expands. A few service-oriented chemical companies will probably seek to compete with the water-treatment companies in their own specialized fields of formulation and service. However, a larger number of companies will develop and sell specialty chemicals in bulk to the water-treatment companies for formulation, service, and distribution.

Supply water treatment

Treatment of bulk supply water for public and industrial use is the second largest segment of the market for chemicals and the list of the principal chemicals used is rather lengthy.

The estimated breakdown of supply water use in the U.S. in 1965 is as follows:

Supply water	Billions of gallons per day
Irrigation	148
Steam electric utilities	119
Industrial and commercial	73
Public water utilities	25
Rural domestic	7
Total	372

Irrigation water is rarely if ever treated, and cooling water for electric ultilities receives relatively little treatment. The market for chemicals is concentrated in the public water utilities and in industrial plants.

Water has traditionally been a cheap commodity—undoubtedly too cheap. The most highly treated type of supply water, that purchased from public water utilities, had an average cost in 1964 of 35 cents a thousand gallons, equivalent to 8.4 cents a ton. Industrial supply water generally costs only 1 to 15 cents a thousand gallons.

Accordingly, the chemicals used until now for treatment of supply water have mostly been such low cost bulk commodities as lime, alum, and chlorine. Sales of these products are increasing at a moderate rate. For example, the reported consumption of lime for water treatment increased from 778,000 tons in 1960 to 964,000 tons in 1965, an average rate of increase of 4.4% a year. However, since water treatment takes only a small percentage of total sales of these heavy chemicals— only 3% in the case of chlorine—most heavy chemical companies are not very active in this market.

More recently a number of specialty chemicals have been introduced for supply water treatment. Among these are biocides, coagulant and filter aids, specialty oxidants, and ion exchange resins. These products sell for considerably higher prices than the traditional heavy chemicals; for example,

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Principal national suppliers of internal water-treatment chemicals and service

Betz Laboratories
Calgon Corp.
Drew Chemical Co., Power Chemicals Div.
Economics Laboratory, Inc., Magnus Chemical Div.
W. R. Grace & Co., Dearborn Chemical Div.
Graver Water Conditioning Co. (subsidiary of Union Tank Car Co.)
Nalco Chemical Co.
North American Mogul Products Co.
Oakite Products
Ritter-Pfaudler Corp., Permutit Div.

Operating data for two leading publicly held companies in water treatment, 1965

	Betz	Calgon	30 Major chemical companies[a]
Sales, $ million	$17.2	$59.5	$592
Expenses, % to sales			
Cost of sales	49.9%	53.8%	64.0%
Selling, general and administrative	36.0	26.9	16.7
Ratios, sales to:			
Net worth	3.1	2.0	1.8
Land, buildings, and equipment (at first cost)	9.2	2.8	1.3
Inventories	11.6	9.5	6.4
Profitability			
% to sales	7.5%	9.3%	7.6%
% to net worth	23.2	18.4	13.0

[a] Average.

polyelectrolyte coagulant aids cost $1–$2 a pound of solids as compared with alum at 2 cents a pound. However, they are generally used in relatively low concentrations to perform tasks that the older heavy chemicals cannot accomplish alone. For example, in water clarification, synthetic polyelectrolytes are generally used at concentrations of 0.25 p.p.m. or less, whereas alum is used at 10 to 85 p.p.m. Sometimes a combination of alum plus a small amount of polyelectrolyte is used. In suitable applications polyelectrolytes can thus be competitive in total cost, and in addition can offer such important advantages as larger and denser floc, more rapid settling, faster filtration, and increased throughput in sedimentation basins.
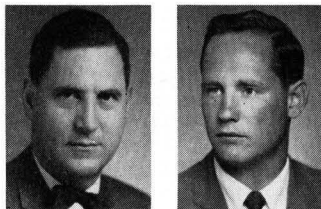
C. H. Kline   **T. S. Bry**

Dr. Charles H. Kline *is founder (1959) and president of Charles H. Kline & Co., Inc. Previously (1949–52), he was manager of product planning in the General Electric chemical division, then (1952–56) manager of the chemical development division of Climax Molybdenum. From 1956–59, Dr. Kline was scientific director at Schulton, Inc. He received his B.A. (1940) and Ph.D. (in physical chemistry, 1944) from Princeton University. The author of numerous articles on technical and management subjects, Dr. Kline is a member of ACS, AAAS, Society of Chemical Industry, Commercial Chemical Development Association, Chemical Market Research Association, and American Institute of Mining, Metallurgical, and Petroleum Engineers.*
Thomas S. Bry *joined Charles H. Kline & Co., Inc., in 1963, having previously worked as a research chemist at Merck & Co. (and later as assistant to the national sales manager of the food products department of that company). Mr. Bry received his B.A. from Middlebury College in 1958. He is co-inventor of many patented drug synthesis processes and author of several articles on chemical markets.*

The consumption of specialty chemicals for supply water treatment is still relatively small, but will increase gradually as quality requirements rise in such areas as taste and odor control, as the pollution load rises, and as suitable new products are developed. A number of basic chemicals manufacturers are active in research in this field. Among the leaders are such companies as Dow, American Cyanamid, Hercules, and Rohm and Haas, which have long experience in developing specialty chemicals for such water-related uses as mineral beneficiation and paper making.

Pollution control

At present pollution control is the smallest segment of the market for chemicals. Until recently there has not been enough pressure from the public to force all municipalities, federal installations (such as Army camps), and industrial plants to treat their wastes. Of course, many of these organizations do treat wastes, but frequently low cost methods are used that do not require chemicals—for example, bacterial digestion of organic wastes, and ponding or lagooning of industrial effluent.

As with supply water treatment, the principal chemicals now used are mostly low cost heavy chemicals, such as ferric chloride, chlorine, lime, and alum. As public demand rises for stricter control of pollution, the consumption of these products is increasing, generally at a much higher rate than in supply water treatment. For example, the reported consumption of lime for treatment of sewage and industrial wastes rose from 132,000 tons in 1960 to 267,000 tons in 1965, an average rate of increase of 15.0% a year, more than three times the comparable rate of increase for lime in influent water treatment.

However, the principal chemical opportunities in pollution control, as in supply water treatment, undoubtedly lie in the development of specialty chemicals tailor-made for particular applications. Of greatest interest are the polymeric coagulant aids, which have found wider utilization in treating effluent wastes and conditioning sludge than in clarifying influent water. Dow Chemical has been particularly active in developing these products. Other leading producers of such products include Hercules, American Cyanamid,

Estimated U.S. market for chemicals in water management in 1966

	Millions of dollars		
	Indus-trial	Munic-ipal	Total
Water treatment			
Internal	$150	a	$150
Bulk supply water	20	$55	75
Waste treatment	15	10	25
Total	$185	$65	$250

a Negligible.

and Rohm and Haas among the basic chemical manufacturers and Nalco and Calgon among the more specialized water treatment companies.

Thus far polyelectrolyte coagulant aids and other specialty chemicals have been used chiefly to improve performance in existing facilities. The main opportunity lies in the development of complete systems designed to exploit the full advantages of these products. For example, Calgon recently announced a new two-step process of waste treatment that can replace the conventional primary sedimentation and secondary bacterial digestion sequence with reported savings of 35% in capital costs and 90% in required land area. The Calgon process uses polymers in the first step to coagulate and settle solids and activated carbon in the second step to filter the remaining solids and adsorb dissolved contaminants. The activated carbon is regenerated periodically by burning off impurities.

A wide variety of other processes for waste treatment are under investigation in government and industrial laboratories. Many of these are radical departures from conventional practice—for instance, the application to wastes of such mineral beneficiation techniques as flotation or liquid ion exchange. A number of processes are concerned with disposal of organic sludges. Two examples are Sterling Drug's Zimmerman process based on wet air oxidation and the Carver Company's oil emulsion process for fatty sludges.

The whole field of pollution control is still in the early stages of development. Local quality standards for effluent water are just now being set by the states to meet the deadline of July 1, 1967, set by the Federal Water Quality Act of 1965. Not one of the radically new processes has yet received wide acceptance. Practically, the only sure data are, first, that pollution control

will increase rapidly both in the number of facilities and in the required quality of effluent waters; and, second, that chemicals will play an increasingly important role in treatment.

Despite its present small size, the pollution control segment of the market has attracted the greatest interest among chemical manufacturers. In addition, the leading water-treatment companies have begun to offer industrial plants comprehensive services in pollution control similar to those they already provide in internal water treatment.

Outlook for water treatment

The overall consumption of chemicals in water and waste treatment is growing at a fairly high rate. The three publicly held companies with high percentages of their total sales in internal water treatment are all expanding rapidly. In the five-year period, 1961–66, Nalco's sales increased 106%, Betz's 85%, and Calgon's 65%. Sales of Culligan, the leader in home water conditioning, increased 135% in this same period.

Internal water treatment should continue to grow for the next few years at a rate considerably above that for the whole economy. An average rate of increase of 12% a year during the next 10 years seems entirely feasible. Consumption of chemicals for bulk supply water treatment will grow much more slowly, probably at an annual rate around 5%.

Consumption of chemicals for pollution control is difficult to forecast because of the rapidly changing quality requirements and methods of treatment. An average rate of increase of 15% a year appears likely.

On this crude basis the market for chemicals in water and waste treatment in 1976 can be estimated very roughly as follows:

	Millions of dollars	
	1966	1976
Internal treatment	$150	$450
Bulk supply water	75	120
Pollution control	25	85
Total	$250	$655

For the chemical manufacturer, a particularly important feature of the overall growth is the change in product mix. Greater acceptance of the newer high-valued products will make water and waste treatment less dependent on heavy chemicals and increasingly a market for specialties.

Chemical sales for internal water treatment and pollution control will increase markedly in next decade
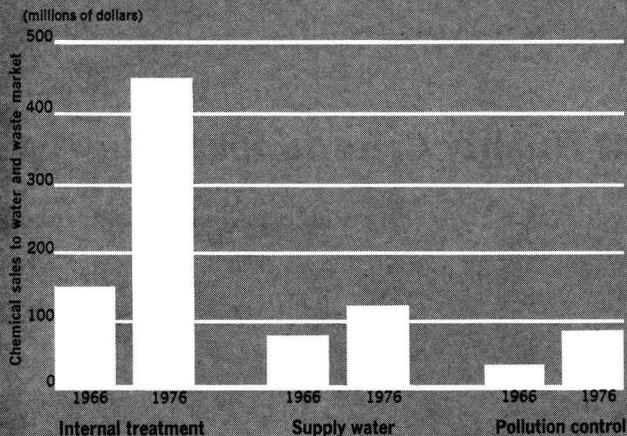
Profitability of water treatment companies exceeds average for 30 chemical companies
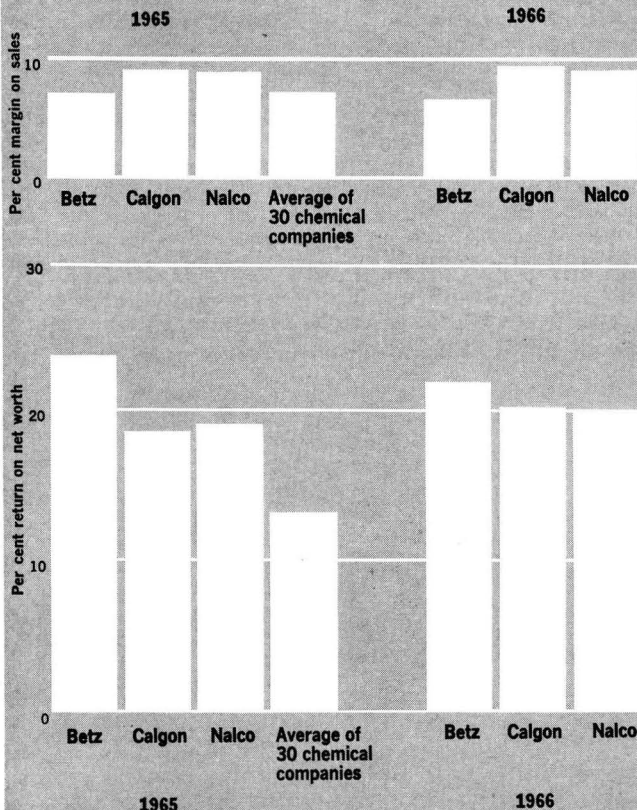
Air Quality Criteria for Sulfur Oxides Set by HEW

In the first of a series of reports setting standards
for air quality, HEW has established the goals;
now haggling over procedures takes precedence

Detectable increases in human illnesses and death begin to occur when the concentration of sulfur oxides in the air averages, annually, 0.015 part per million. Yet this level is exceeded in virtually all major American cities, and in many smaller ones.

These startling facts are presented in a government report, *Air Quality Criteria for Sulfur Oxides*, issued by the Department of Health, Education, and Welfare's Public Health Service on March 22, 1967. The 260-page report is a response to the Clean Air Act of 1963, which requires HEW to publish criteria based on the latest scientific knowledge on the effects of pollutants in the atmosphere. The report is the first in a

series that is slated to cover all of the major air pollutants in the U.S. today. Subsequent reports will set standards for such things as particulate emissions, photooxidants, hydrocarbons, carbon monoxide, and nitrogen oxides.

The HEW report emphasizes that the sulfur dioxide effects which are indexed do not derive solely from the presence of sulfur oxides in the atmosphere. These effects are, for the most part, those observed when sulfur oxides (at various concentrations) have been present in the atmosphere. Because of the interactions between pollutants and the reactions of pollutants with both oxygen and water in the atmosphere, and because of the influence of sunlight

and temperature on these reactions, the real or potential hazards of one atmosphere polluted with oxides of sulfur may be quite different from the real or potential hazards of another atmosphere similarly polluted with oxides of sulfur.

Health effects

Specifically, *Air Quality Criteria for Sulfur Oxides* cites as significant human health effects of sulfur dioxide, sulfuric acid, and sulfate salts, individually and collectively, such maladies as bronchoconstriction, increased airway resistance, and increased respiration and pulse rates. These sulfur compounds are well known for their irritant action on the

Sulfur dioxide and sulfuric acid mists reduce visual range

Sulfuric acid mist/sulfur dioxide ratios increase as relative humidity rises
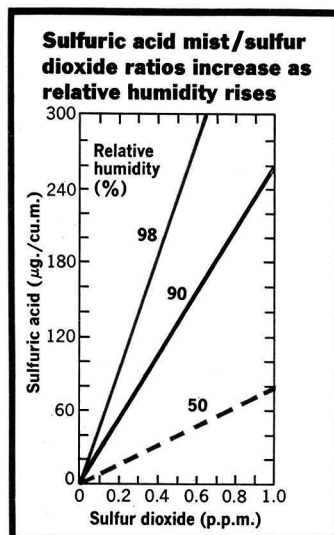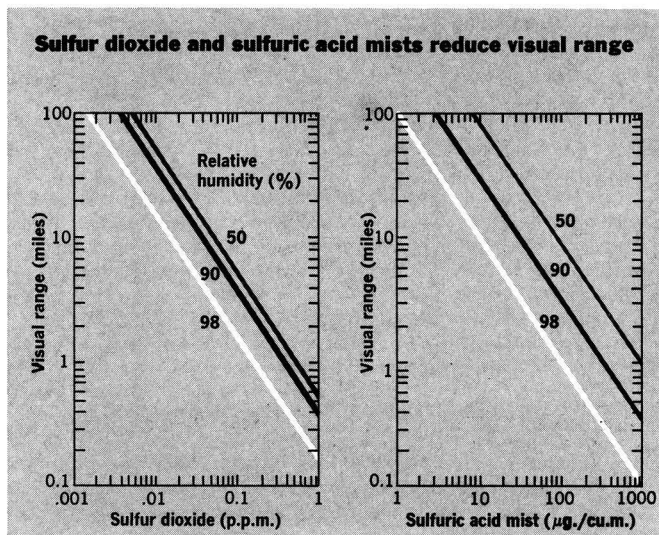
mucous membranes of the respiratory tract. The action is associated with thickening of the mucous blanket, increased secretion of mucous, and reduced ciliary activity.

Bronchitis attack rates in man may be quadrupled by sulfur oxide concentrations of 0.5–1.0 p.p.m. persisting for several days. Death rates from heart and respiratory tract conditions rise during severe air pollution involving sulfur oxides.

Vegetation effects

The Public Health Service criteria set the threshold for acute injury to vegetation at levels several times higher than that for human beings—0.28 p.p.m. sulfur dioxide for 24 hours, or 0.48 p.p.m. for four hours, or any combination of exposure time t and concentration c in which $(c - 0.24)t = 0.94$.

Even in areas with very low average annual concentrations, acute plant damage can occur if emissions from large single sources result in threshold or greater exposures for short periods. In one area under study, 36% of the gardens showed plant injury at an annual average concentration of 0.009 p.p.m. sulfur dioxide with a maximum daily average of 0.155 p.p.m. When peaks of sulfur dioxide concentration reached levels of 5–10 p.p.m., 89% of the gardens showed plant injury even though the area had only 0.033 p.p.m. average annual concentration and maximum daily average sulfur dioxide levels of 0.60 p.p.m.

Visibility effects

Transmission of light, which is restricted by, among other atmospheric phenomena, the light-scattering properties of sulfuric acid mist and sulfate salts, leads to a decrease in visibility. This decrease becomes more severe as humidity increases, not only because
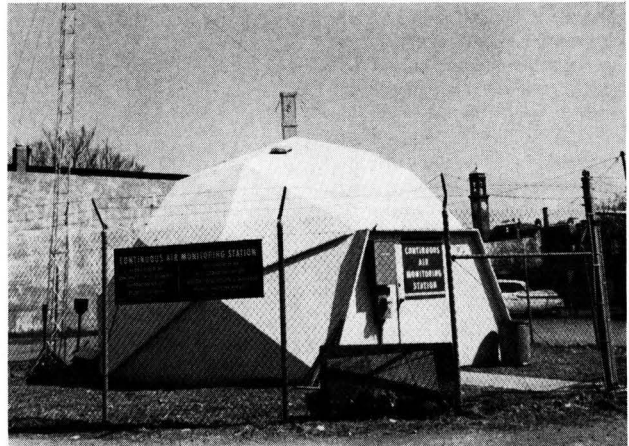
Data from the Continuous Air Monitoring Program (CAMP) were used in setting the criteria for sulfur oxides recently published (in Air Quality Criteria for Sulfur Oxides) by HEW. CAMP stations provide continuous automatic measurement of seven important air pollutants: carbon monoxide, nitric oxide, nitrogen dioxide, ozone, total oxidants, total hydrocarbons, and sulfur dioxide.

In addition, the stations collect related data on gaseous and particulate air pollutants. A carbon-filter device samples the air for total gaseous pollutants. The air is pulled through a filter of activated carbon that presents an extensive surface area to which the gases cling. The gases are released from the filter in the laboratory and analyzed by various chemical means.

High volume air samplers—the instruments used in the National Air Sampling Network—are also operated at each CAMP station. These instruments measure particulate matter at more than 250 locations in the U. S. and are very reliable.

Tape-filter samplers are operated as soiling indicators. As sample air is drawn through these filters, the pollutant particles produce a darkened spot.

Each CAMP station also has an automatic precipitation sampler which has a lid that opens when activated by moisture and closes when precipitation stops. Thus, only the pollutants washed in by precipitation are measured.

Turbidity, the darkening or obscuring property of the atmosphere, is measured by a sun photometer aimed at the sun to determine its intensity. Since pollutants diminish the intensity of light between the sun and the photometer, the photometer provides a sensitive measure of total pollutants in the air.

Wind speed and direction, temperature, humidity, barometric pressure, cloud cover, and visibility are all recorded on other automatic devices so that their effects upon pollution concentrations can be noted. CAMP stations, such as this one (located in Washington, D. C.), are operated in Denver, St. Louis, Chicago, Philadelphia, and Cincinnati.

ห้องสมุด กรมวิทยาศาสตร์

of the increased humidity itself, but also because of the increased interaction between the sulfur compound pollutants and the moisture in the air.

The HEW document does not fix any threshold at which visibility reduction begins. Rather, HEW simply charts visibility range as a function of sulfur pollution concentration and relative humidity. At a pollution level of 0.1 p.p.m. sulfur dioxide and a relative humidity of 50%, for example, the visibility range is approximately five miles. If the pollution level reaches 0.2 p.p.m. sulfur dioxide, visibility is reduced to less than two miles.

Materials effects

Corrosion of carbon steels, zinc, and copper begins with only trace amounts of sulfur pollution in the atmosphere. As might be expected, the corrosion rate increases as sulfur pollution levels build. Stone statuary and buildings, paper, leather, textiles, and painted surfaces all suffer varying degrees of damage that are related to the levels of the sulfur compounds in the atmosphere.

From these data on animals, plants, and materials, HEW draws the conclusion that if sulfur oxides are reduced to levels that protect health, the effects on vegetation will be eliminated, visibility will be appreciably improved, and damage to fabrics, metals, buildings, and the like will be markedly reduced.

The criteria

For about five years prior to publishing its standards for acceptable air criteria, HEW's Public Health Service monitored the air in several urban communities. From data collected from its Continuous Air Monitoring Program (CAMP) in these cities, PHS says that it can use the average data to set air quality standards. Where the average annual concentration of sulfur dioxide in the atmosphere is 0.015 p.p.m. in

Sulfur oxides pollution has a measurable effect upon health . . .

Range of concentrations and exposure times in which deaths have been reported in excess of normal expectation

Range of concentrations and exposure times in which significant health effects have been reported

Ranges of concentrations and exposure times in which health effects are suspected
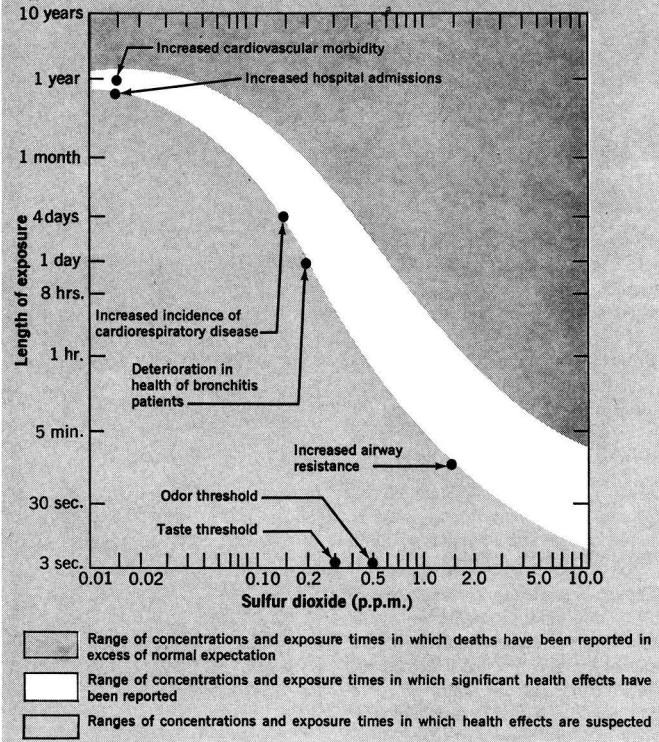
Sulfur dioxide is released to the atmosphere from a variety of sources

Process	Sulfur dioxide[a]	
	Tons	Per cent of total
Burning of coal (total)	14,029,000	60.0
Power generation (211,189,000 tons)	9,580,000	41.0
Other combustion (112,630,000 tons)	4,449,000	19.0
Combustion of petroleum products (total)	4,817,000	20.7
Residual oil	3,703,000	15.9
Other products	1,114,000	4.8
Refinery operations	1,583,000	6.8
Smelting of ores	1,735,000	7.4
Coke processing	462,000	2.0
Sulfuric acid manufacture	451,000	1.9
Coal refuse banks	183,000	0.8
Refuse incineration	100,000	0.4
Total	**23,360,000**	**100.0**

[a] A small amount of this tonnage is converted to sulfur trioxide and sulfuric acid mist before discharge to the atmosphere.

Source: F. A. Rohrman and J. H. Ludwig, "Sources of Sulfur Dioxide Pollution," Presented at the 55th National Meeting of the American Institute of Chemical Engineering, Houston, Tex., Feb. 7–11, 1965. Session No. 46, Paper No. 46e, pp. 1–16.

... And a demonstrated impact upon vegetation

Range of concentrations and exposure times in which injury to vegetation has been reported

Range of concentrations and exposure times of undetermined significance to vegetation
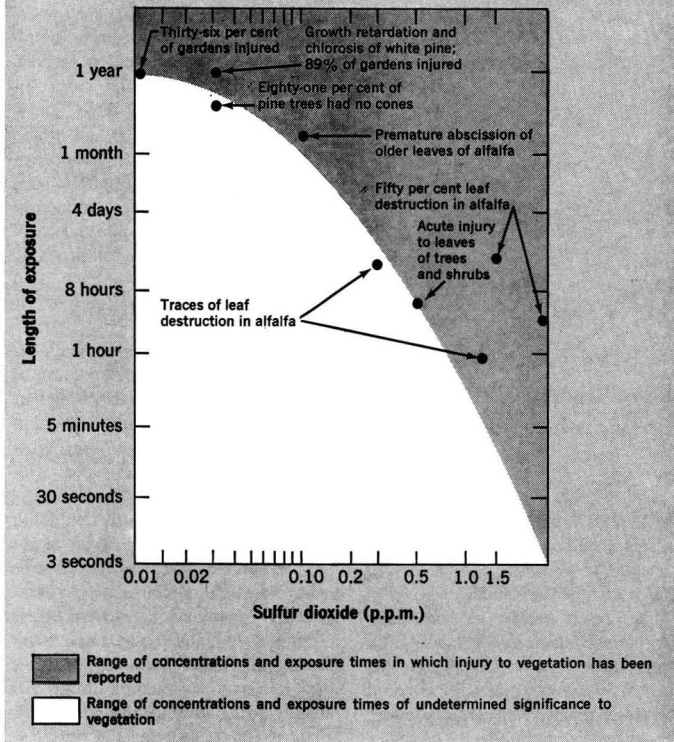
urban communities that have diverse sources spewing sulfur compound contaminants into the atmosphere—and combining these data with effects on plant and animal life in the test communities—HEW concludes that the following sets of ranges of sulfur dioxide concentrations can be used as criteria for acceptable air quality:

Time period	Maximum	1 Percentile
24-hour average	0.05–0.08	0.04–0.06
1-hour average	0.12–0.20	0.05–0.11
5-minute average	0.10–0.50	0.05–0.14

Special cases

Despite the implied limitations on maximum sulfur dioxide in an area with an annual average concentration no greater than 0.015 p.p.m., the fact is, according to the report, that special circumstances occur where atmospheric sulfur dioxide concentrations are considerably wider ranging than the average data suggest. For example, because of seasonal space heating needs, seasonal

variations in sulfur oxides emissions may be greater in some cities than in CAMP cities. In those cities where seasonal space heating needs show wide variation, the ratios of short-time averages to annual averages are greater than in CAMP cities and, consequently, more severe sulfur oxides effects are expected. In such communities, according to HEW, the average concentration

Physical constants of sulfur dioxide

Molecular weight	64.06
Density (g./l.) (gas)	2.927 at 0° C.; 1 atm.
Specific gravity (liquid)	1.434 at −10° C.
Molecular volume (ml.) (liquid)	44
Melting point (° C.)	−75.46
Boiling point (° C.)	−10.02
Critical temperature (° C.)	157.2

during the seasonal or semiannual period of highest sulfur oxides emission, rather than the annual average, should be used as the basis for estimating likely-to-develop concentrations and consequent deleterious effects during those periods.

In areas affected by large, single sources, average sulfur dioxide concentrations are frequently below the detectable level. However, measurably high concentrations occur briefly from time to time. In such areas, the taste and odor of sulfur dioxide are of prime concern to the inhabitants of the community. Nonetheless, control measures designed to alleviate these unpleasant sensations should also prevent more serious health effects.

Industry reaction

Naturally, the kind of reception accorded the HEW report has been mixed. Spokesmen for the coal, petroleum, and electrical utility industries brand the sulfur dioxide criteria economically unrealistic, scientifically indefensible, and technologically impossible. The chemical industry, which has a smaller though significant stake in the matter, is reserving comment, pending study of the criteria and the methods HEW used to develop them.

The coal industry has been the most vocal in its criticism of the new criteria. Spokesmen for the industry charge that the health citations meant to justify HEW's conclusions are, in many cases, incomplete, vague, and used out of context. To support these allegations, they offer a critique prepared by Hazleton Laboratories (Falls Church, Va.), which holds that those who prepared the criteria misused the data and reached unjustified conclusions.

On the other hand, manufacturers of filters, gas monitoring equipment, and purveyors of low-sulfur-content fuels, to name just a few industries, welcomed the report.

Man reacts to sulfur oxides pollution at concentrations as small as 0.5 p.p.m.

Procedure used	Threshold concentration			
	H_2SO_4	SO_2[a]	$H_2SO_4 + SO_2$	
	µg./cu.m.	p.p.m.	µg./cu.m.	p.p.m.
Threshold concentration of irritation effects and odor perception	600–850	0.5–0.9	300	0.17
Data obtained by the method of eye adaptation to darkness	630–730	0.31	300	0.17
Data obtained by the method of optical chronaxy	730	0.50	600	0.40
Encephalographic method	630	0.30	300	0.17
Electrocortical conditioned reflex	400	0.20	150	0.17
			300	0.08

[a] A factor of 0.33 has been used to convert mg./cu.m. to p.p.m.

Source: K. A. Bushtueva, "New Studies of the Effect of Sulfur Dioxide and of Sulfuric Acid Aerosol on Reflex Activity of Man," "Limits of Allowable Concentrations of Atmospheric Pollutants," Book 5, Ryazanov, V. A., ed. Levine, B. S., trans. U.S. Department of Commerce, Washington, D.C., March 1962, pp. 86–92.

CAMP. *Sulfur dioxide is measured at the CAMP stations by an automatic instrument, the Beckman SO₂ Analyzer. Polluted air is drawn through an acidic hydrogen peroxide solution, which converts sulfur dioxide to sulfuric acid. The resulting solution flows through a sample cell, and the difference between the conductivity of the sample cell and a reference cell indicates the amount of sulfur dioxide in the air. Mr. George Walsh (left) of the Washington, D.C., CAMP station calibrates the analyzer; Mr. Charles Brunot (below), Program Chemist, charts the SO₂ levels calculated by the instrument*

If attacks on the HEW report with its sulfur dioxide criteria seem strange in light of the fact that HEW has no statutory authority to set air quality standards, consider that almost simultaneously with release of the report, HEW announced pollution curbs for federal installations in three major cities—New York, Chicago, and Philadelphia. Such curbs will increase operating costs for these facilities by 15 to 20% per year. Furthermore, the numerous municipal, state, and interstate air pollution control agencies will probably refer to the report, using it as a guideline in formulating local laws regarding air pollution.

With estimated costs for ending air pollution running into the billions of dollars, it is not the least surprising that industry is concerned about the portion of these costs it will have to bear. Now that the first step has been taken with the publishing of sulfur oxides criteria— and with the promise of more air quality criteria to come—there is little doubt that a round robin involving government, industry, and consumer has been started. Protests against governmental interference, higher costs of doing business, increased prices for consumer products, or the slowness of government in setting air quality standards will crisscross the nation for the next few years. But the mood of the U.S. citizen, reflected in Congress, is to control air pollution. The goal is established; the haggling over procedures now takes precedence.

Activated Carbon Used for Large Scale Water Treatment

Effective for both water purification and pollution abatement, granular activated carbon treatment systems offer economies that derive from their high throughput and regeneration qualities

Donald G. Hager *Calgon Corp., Pittsburgh, Pa. 15230*

The first full scale granular activated carbon water purification plant of its kind in the world has recently gone on-stream at Nitro, W. Va. Culminating three years of related research and design studies, plant managers point out that the plant supplies more than 8 million gallons of pure water daily to approximately 13,000 residents of Nitro, Dunbar, and South Charleston, W. Va.

The principal features of the new water purification system are: replacement of sand with granular carbon in the plant's filter beds to achieve simultaneous filtration of turbidity as well as adsorption of organic materials; and on-site reactivation of the carbon.

The ability of charred substances such as wood char, bone char, or charcoal to remove undesirable tastes and odors from water has been known for many years. A literature search reveals that real efforts, some partially successful and others not, were made at water purification using these materials in filter beds.

The successful use of animal charcoal for filtering the East London Water Company's water in lodging houses with 700 occupants in Columbia Square, London, in 1866 led to public demand for its use on a larger scale. Some advocated filtering the entire London supply through beds of animal charcoal.

Byrne, in 1866, investigated the use of charcoal and bone char for water filtration and concluded that it was not suitable for a large supply. Efforts in the U.S. during the early 1930's toward large scale filtration-purification resulted in similar findings.

These early evaluations were based upon charcoal which had relatively little adsorptive capacity compared to present day activated carbon products. Furthermore, the modern practice of reactivating spent granular carbon for many cycles of reuse has completely changed earlier conclusions regarding economics of granular carbon for water treatment.

Coal-based granular carbon combines density with hardness, making it the preferred material for reactivation procedures. In addition, these same properties make coal-based carbon useful in conventional water filtration equipment.

The use of granular carbon in place of filter media such as sand or coal in the purification of municipal water supplies is a recent development of Pittsburgh Activated Carbon Co., a wholly-owned subsidiary of Calgon Corp. The technique of simultaneous adsorption-filtration was pioneered in 1962 in Hopewell, Va., at the Old Dominion Water Co., a subsidiary of American Water Works Co. Application experience at Hopewell has since been applied in other water plants with added refinements such as on-site reactivation. The Nitro plant of the West Virginia Water Co. is an example of this type of complete system.

The Kanawha River, which serves as the source of water for the Nitro plant, is heavily polluted with various organic industrial wastes. For many years, water plant officials tried to improve the finished water while upstream industries attempted to minimize pollution loads. Nevertheless, in spite of double aeration and relatively high powdered carbon and chlorine addition at the water plant, the odor and carbon-chloroform extract (CCE) values frequently exceeded the recommended levels. Because of this odor problem, the company officials agreed to conduct a large-scale experiment with granular activated carbon which led to development and construction of the full-scale system.

During 1963, a series of small-scale experiments and a plant-scale test were conducted to obtain granular carbon design data for removal of odorous and nonodorous organic material from Kanawha River water.

An accompanying illustration gives a flow chart of the original purification system and the revisions made for the plant-scale experiment. The principal change for the Nitro test was discontinuance of powdered carbon addition. Also, two full-scale carbon beds were added following the sand filters. (The carbon beds were housed in rebuilt gravity sand filter structures.)

Data derived from both the large- and small-scale tests led to the following conclusions:

• Granular carbon removed both the odorous and nonodorous organic material to meet the recommended

Granular carbon purification system

Dewatering screw conveyor

(1) Filter being filled with reactivated carbon

(2) Filter being backwashed to:
- Clean out carbon bed to remove turbidity.
- Settle and even out carbon bed after filling.

(3) Filter that has been filled with carbon and which is now being used as a final filtering operation to remove objectionable taste and odor from the water prior to its being pumped to consumer

(4) Filter in which the spent carbon is being removed for reactivation after which it can be reused in the system

Regeneration furnace

Carbon make-up hopper

Make-up carbon 60-pound bag

To drain

Carbon slurry tank

Quench tank

Eductor

Water lines

Eductor

Overflow

To river

Grade

Gravel bed

Spent carbon

Eductor and hoist

Traveling trolley

Pipe gallery

Water from main supply

Main shutoff valve

Reactivated carbon

Spent carbon

Collector pipes in bottom of cell

Equipment Summary

Adsorption—Filtration Equipment

Number of Units — 10

Type — Gravity flow, concrete, filter boxes

Underdrain System — Pipe Laterals

Media Support — Graded Gravel

Media — 30″ Bed MWT (14x40 Mesh) Granular Carbon
 — effective size 0.60 mm
 — uniformity coefficient 1.7

Flow Rates — 1-2 gpm/ft²

Backwash Rate — 10 gpm/ft²

Granular Carbon Reactivation Equipment

Total Space Requirement — 400 ft²

Furnace — 8 hearth, 6′0″ OD x 4′6″ ID
 — Nominal Capacity — 500 lbs/hr

Furnace Feed System
 — 8′0″ diameter x 8′0″ cone bottom slurry tank
 — rotary vane feeder/water eductor
 — dewatering screw conveyor

Carbon Return System
 — 2′0″ x 2′6″ cone bottom stainless steel carbon quench tank
 — water eductor

Carbon Transfer Lines
 — mild steel pipe and flexible rubber hose

standards of the U.S. Public Health Service.

• Standard size, 8 × 30-mesh, granular-activated carbon beds were able to produce an odor-free water as the raw water threshold odor number varied from 300 to 1300.

• A finer carbon, 20 × 50-mesh, produced an odor-free water for twice as long as the standard size carbon.

• Within the tested range of physical and hydraulic conditions, a linear relationship existed between contact time and carbon performance.

• When the threshold odor number was reduced to less than 3, the carbon-chloroform extract value was reduced to less than 200 p.p.b., the recommended maximum value.

This successful test work was reviewed and approved by the U. S. Public Health Service and was reported in a paper titled, "Carbon Bed Design Criteria Study at Nitro, W. Va."

Hopewell experience

Experimental work at the Old Dominion Water Co. in Hopewell, Va., during 1963–64 revealed that granular carbon could be used in place of sand in conventional filters. The granular carbon beds, still in use, are 2 feet deep and operate at a nominal water flow rate of 2 gallons per minute per square foot. In an earlier paper with M. E. Flentje (1965), we reported that iron, manganese, and turbidity were reduced to levels equal to, or better than, those of sand media of the same or smaller effective size. Odor removal in the carbon beds was essentially complete while comparative sand filters were, as expected, not effecting odor removal.

Nitro water purification plant

The complete granular carbon purification system at Nitro resulted from previous test work at both Nitro, W. Va., and Hopewell, Va. As designed, it is the first full-scale plant of its kind in the world. The plant has a nominal capacity of 15 million gallons per day and produces close to 8 million gallons per day on a yearly average. Raw Kanawha River water is first double-aerated to remove volatile contaminants. Following aeration, the water enters a 24-hour sedimentation basin where alum is added to effect coagulation and chlorine is used for disinfection purposes. After coagulated impurities have settled out, the water enters filter beds of granular-activated carbon. The carbon beds remove any remaining suspended matter, as well as tastes and odors, from the water. Post chlorination completes the treatment prior to distribution.

The Nitro filters are conventional rapid sand gravity units equipped with pipe lateral underdrain systems. However, the filter sand has been replaced by 14 × 40-mesh granular carbon. Carbon is supported above the underdrain system by coarse gravel. The granular carbon removes both turbidity and dissolved organic contaminants which persist through the prior treatment sequence. Eight filters are onstream in parallel operation with the effluents of each blended to produce a finished water of the highest quality.

The total carbon system includes dual-purpose granular carbon filters, carbon handling equipment, and a multihearth, high temperature furnace for on-site reactivation of the granular carbon.

Reactivation of the spent granular carbon begins with its removal as a water slurry from the filters. Excess water is drained from the carbon in special dewatering equipment and the carbon fed to the furnace where it is subjected to temperatures in the 1600° to 1800° F. range. The adsorbed organic impurities are burned from the carbon thus reactivating the granular carbon for another adsorption cycle. The carbon is then quenched in water and returned as a water slurry to the filters for reuse.

The following table presents test results obtained at Nitro during the period September–December 1966:

Flow diagram of Nitro, W. Va., water purification plant

Original system

Raw water
Kanawha River → Double aeration → Coagulation and sedimentation → Filtration → Clearwell → Distribution system
Powdered carbon slurry ⋯ Alum ⋮ Chlorine

Experimental system

Raw water
Kanawha River → Double aeration → Coagulation and sedimentation → Filtration → Clearwell → Granular carbon beds → Clearwell → Distribution system
Alum ⋮ Chlorine ⋮ Chlorine

New system

Raw water
Kanawha River → Double aeration → Coagulation and sedimentation → Granular carbon beds → Clearwell → Distribution system
Alum and chlorine ⋮ Chlorine

	Raw water	Applied to filters	Recommended standards	Finished water
Threshold odor number	66–333	30–50	<3	0–3
Turbidity (Jackson turbidity units)	...	5–15	<5	<0.05
Carbon-chloroform extract value (p.p.b.)	...	>200	<200	<50

Based upon four months' operation, the following additional conclusions have been reached:

• The carbon beds can stay onstream prior to reactivation 50% longer than designed, resulting in greater operating economy.

• No additional labor is required to operate the granular carbon system—including the reactivation equipment.

• The same backwashing procedures used for sand can be used effectively for the granular carbon beds.

Design criteria

In general, granular carbon can be used after conventional filtration of suspended matter or as a combination filtration-adsorption medium. Granular carbon has been utilized in conventional rectangular or circular rapid sand filters, in pressure vessels, and in specially designed adsorbers. The choice of equipment depends upon the severity of the organic removal problem, the availability of existing equipment, and the desired improvement of adsorption conditions.

Usually, two or more units are used in parallel downflow operation. Startup of the units is staggered so that exhaustion of each bed will not interrupt continuous operation. Blending of the fresh carbon effluent with partially exhausted carbon effluent prolongs the usefulness of the bed before reactivation or replacement of the individual beds is necessary.

Flow rates are usually 2.5 to 5 gallons per minute per square foot and bed depths are varied accordingly. Combining these two factors can be thought of as adjusting the contact time of the water with the granular carbon beds. We have noted that a direct linear relationship exists between contact time and carbon bed performance at various installations on both water and waste treatment systems.

When the granular carbon bed is functioning both as a turbidity removal and adsorption unit, there may be reasons to limit the bed depth and flow rate parameters to remove turbidity effectively and to provide proper filter backwash. If granular activated carbon

is to be effective in turbidity removal, it must be hard enough to withstand vigorous backwash agitation. At the same time, it should be dense enough to expand without loss during the backwash cycle and to settle quickly for immediate resumption of filtration. Coal-based granular carbon possesses approximately the same density and filtration characteristics as anthracite coal, which has found increasingly wider use in the water-treatment field.

Particle size of the carbon, in addition to contact time, should be considered carefully as a design factor. Reduction of particle size for a given set of flow conditions is one recognized means of increasing adsorption rate leading to improved adsorption performance. Reduction in particle size to improve adsorption must be consistent with other significant factors. For example, if too small a particle size were selected, length of filter run in the adsorption-filtration bed would be too short. Also of design consideration is that the reactivation of extremely small granular carbon can present handling problems as well as excessive losses.

Granular carbon water reclamation

A number of granular carbon installations are processing municipal, industrial, and commercial wastes. The reclamation objective varies between complete renovation of the waste to pollution abatement, to a combination of product recovery–pollution abatement. As would be expected, the pretreatment used in each case and the final organic content of the effluent vary in accordance with the treatment objective.

At Lake Tahoe, Calif., a commercial-scale granular carbon plant (Culp and Slechta, 1966) is being used to purify municipal wastes. Complementing an existing activated-sludge secondary treatment plant, the carbon beds are a part of a tertiary treatment system which effects almost complete removal of suspended matter and organic contamination from the water.

There are specific applications on industrial waste where recovery of valuable by-products is feasible. Removal of the adsorbed product is normally accomplished by means of a chemical which is contacted with the carbon. The chemical treatment step can be accomplished in the adsorbers with appropriate modifications or the

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with Pittsburgh Coke and Chemical Co. Mr. Hager received his B.A. from Grinnell College (1954) and his M.A. in business administration from the University of Pittsburgh (1959). He was also a Fellow of Mellon Institute of Industrial Research. He is credited with developing the first commercial scale application of granular activated carbon for municipal sewage treatment (Lake Tahoe, Calif.) and potable water treatment (Nitro, W. Va.). Mr. Hager is a member of ACS, American Water Works Association, and Water Pollution Control Federation, where he was recently appointed to the Technical Practice Subcommittee on Tertiary Treatment.

saturated carbon can be removed to a separate processing operation. Isolation of the product from the chemical is then accomplished in subsequent steps. Restoration of the carbon's adsorptive capacity is normally not complete for each chemical treatment cycle and thermal reactivation or replacement with virgin carbon is eventually necessary.

Application of the granular carbon adsorption-filtration technique has immediate industry-wide application. For those water purification plants experiencing minor, yet bothersome, taste and odor problems, existing filters can be emptied of sand and refilled with granular carbon. In many instances, reactivation and handling facilities may not be necessary. For others an adequate solution may be provided by adding granular activated carbon beds to the existing treatment process.

Of the numerous unit processes which have been evaluated for advanced treatment of waste water, granular activated carbon adsorption has been demonstrated as the most efficient in terms of organic removal to provide a high quality effluent.

Significantly, the Nitro installation has resulted in both water purification and pollution abatement. Spent powdered-carbon containing adsorbed organic contaminants is no longer discharged to the river after use. Polluting materials are now destroyed in the reactivation furnace and the regenerated granular carbon is returned to the filters for reuse.

Selected additional reading

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QUOTE . . .

Countering Air Pollution in the U.S.S.R.

...During the past 10–15 years, when air pollution grew to become one of the particularly acute social problems throughout the world, intensive research began on ways of cleansing the air. In the U.S.S.R. about 40 institutes and laboratories study this subject.

At the present time our cities are not so strongly subject to smoking. Nevertheless scientists press the search for methods of neutralizing harmful effects of internal combustion engine exhausts. The State allots appreciable resources to research, to the making of special apparatus (neutralizers), and carrying on of different experiments. These resources are being increased in the next five-year period, in part and in connection with the recommended sharp expansion of the country's automobile fleet. Even in our country the problem of sanitizing the air of our cities becomes pressing.

We are talking with the head of the Central Scientific-Research and Design-of-Experiments, Laboratory of Neutralization and Problems of Automobile and Tractor Energetics, Honored Science and Technology Worker of the U.S.S.R., Professor I. Varshavsky. He observes:

"The growth of the vehicular fleet need not be feared for we are proposing measures for elimination of the harmful consequences of engine operation. Only one thing is needed—that agencies and departments affected put into strict practice the measures determined by judgments of the directing organs of our country."

There are not a few ways to fight against toxicity of the waste gases. One may use special fuel additives. But these are not fully effective inasmuch as they work selectively—only on some of the substances. A device may also be attached to the engine's exhaust pipe for cleansing the gas by further burning that gas incompletely burned at high temperatures. Such devices are called thermal or flame neutralizers. There are also those where the products of incomplete combustion pass through a special liquid, joining with it in a reaction. . . .

. . . Our means of persuasion lag; advertising is essentially absent. It is evident that this question must have the attention of press, television, and all the other means of communication now in science and technology.

However, methods are needed not only for persuading but also for compelling. Health agencies together with other organizations must work out toxicity standards for automobile engine exhaust gases and, as well, methods of control which would expediently be placed on government automobile and medical inspections. . . .

. . . All the same a beginning has been made and we must look to its furtherance. This we envision as follows: toxicity standards for waste gases on the whole, obligatory observance of standards by all auto industries and automobile fanciers, checks on an all-Union scale. No matter to whom it belongs, as every motor vehicle is prohibited from operating without an annual technical inspection, so quarterly, the exhaust gases toxic characteristics must be examined with the aid of gas analyzers set on special stands. . . .

Translated by **NORMAN PRECODA**

NOISE

Called the environmental insult, the noise around us grows ever more intense
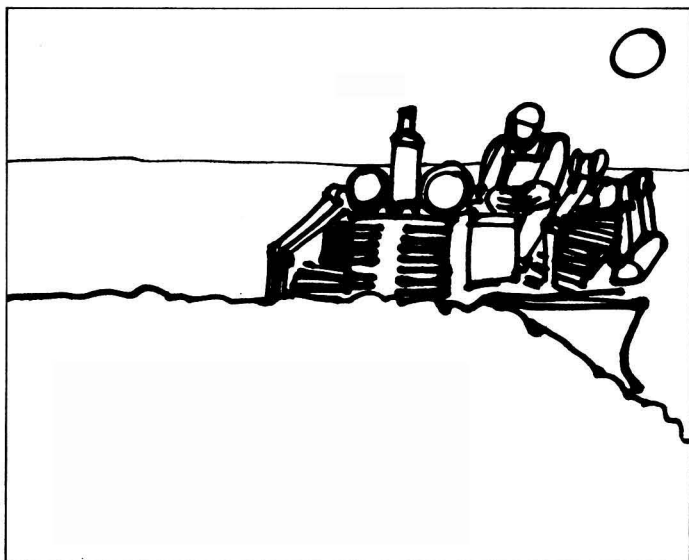
Din, din, din is the cry uttered by a character in Rudyard Kipling's well known poem. But it also is the cry of modern man as he seeks ways to modify the cacophonous environment that seems to go hand-in-hand with civilization

Universities, along with industry and government, have sadly neglected their social responsibility in the field of environmental engineering. Nowhere has the academic community been training sufficient numbers of people in the technical problems posed by various types of pollution in our cities.

In this article we will consider only one of the pollutants of our atmosphere—noise. The reason for being concerned with noise is the same as that for being concerned with other pollutants—it affects people adversely. Some of these effects are reviewed here, together with methods of noise control that may make all communities more pleasant and more healthful places in which to live.

Noise control

But first, what is meant by the terms *noise* and *noise control?* By *noise* we mean any sound which is unwanted. According to this definition, music in your apartment is noise in your neighbor's apartment, making the reasonable assumption that he doesn't want to hear it. *Noise control* is the technology of achieving an acceptable noise environment consistent with economic and operational considerations.

Thus, noise control is concerned with the attainment of acceptable noise conditions—not necessarily with noise reduction. For example, no actual reduction of noise in a shipyard may be involved when acceptable noise conditions for workers are achieved by the use of earplugs. In some cases, it may even be advantageous to achieve acceptable conditions by increasing the noise level!

Consider the following problem. The partition that separates a private office from an adjoining reception area provides insufficient sound insulation so that conversations in the office can be overheard in the reception area. Acceptable conditions might be obtained by improving the noise insulation value of the partition. But a possible alternative solution is simply to increase the noise level in the reception area by the installation of a noise source, such as a fan. The fan noise will mask the conversations that would otherwise be overheard. Thus, the terms *noise control* and *noise reduction* are not always synonymous.

Another example of noise control oc-curs when an airport, whose operations are interfering with the sleep of home owners in the neighborhood, changes its schedule so that there are no evening flights. No actual noise reduction has taken place, but an acceptable noise level has been achieved.

A noisy environment and man

We are interested in noise control and noise reduction because noise may damage hearing, it may affect sleep, or it may produce other physiological responses that are more difficult to measure. For certain types of tasks noise may affect a worker's efficiency; it affects man's ability to communicate through speech; it may produce a feeling of fatigue; and, certainly, it can be a source of considerable annoyance and complaint—especially if one has the feeling that the noise is unnecessary. All of these effects of noise as a form of air pollution are of considerable economic and social importance.

It has long been known that intense impulsive noises—such as explosive sounds—may cause partial or total loss of hearing. However, it is only in recent

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years that a quantitative relationship has been established between hearing loss and daily exposure (for a period of many years) to loud noises that are relatively continuous in duration. There is no discrete step above which exposure to such noise will produce impaired hearing, and below which exposure may be considered safe.

The length of exposure, character of the noise, and many other factors are of importance. Furthermore, there are marked individual differences. The effect of various noise exposure times on possible damage to the ear can be plotted (as shown on an accompanying chart), revealing damage risk contours for noise to which an individual is exposed once per day. These contours indicate noise levels that are considered safe as regards hearing loss for daily exposure of more or less continuous (that is, not impulsive-type) noises.

In order to make use of such a chart, the noise is first measured with an octave-band analyzer. Then, the appropriate contour indicates the sound pressure level that is probably safe for that octave band. For example, if one is exposed to a noise for 60 minutes a day, the sound pressure level in the octave band from 300–600 c.p.s. should not exceed 100 db.

What happens to a wage-earner who works year in and year out in a noise-polluted environment that greatly exceeds these limits? The probability is high that he will sustain a permanent hearing loss due to this noise exposure. Some present estimates are that the total of claims involving compensation for loss of hearing resulting from noise exposure is in excess of $1 billion in the U.S.

When compensation laws were first enacted, benefits were awarded to a worker if an injury reduced his ability to earn a living. According to this wage-loss concept, a worker was entitled to very little compensation if he lost a large percentage of his hearing as a result of working on a noisy punch press for many years, assuming there had been no loss in his ability to earn a livelihood. Management usually has taken the posi-

tion that if this concept is changed there will be no reasonable basis for courts to decide how much compensation to award.

On the other hand, labor has challenged the wage-loss concept, arguing that if a worker loses his hearing because of work in a noisy environment, even if normal hearing is not essential to his job, he should be compensated, since his capacity for enjoying a full life has been reduced. But there are many problems involved in arriving at an equitable solution.

Many such claims may not be justified since the worker may have had a hearing loss before he started work for his employer or he may have sustained the loss from other causes. Also, the losses he claims may be only temporary and he may recover completely if he transfers to work in a quieter environment.

For these and other reasons the courts are proceeding with caution. While this situation has not been resolved completely, it has spurred many employers into taking action to reduce noise levels in their plants, and to provide workers with adequate noise protective devices.

The reactions of a neighborhood or an entire community to city noise are much more complex than the reactions of individuals to noise. Factors in addition to overall noise level that determine whether a noise source is objectionable in a community include the following:

- The acoustical characteristics of the noise and whether the noise occurs during the night or day.
- The number of times the noise source is heard per hour, the background noise level in the community.
- Whether the noise is entirely unnecessary.
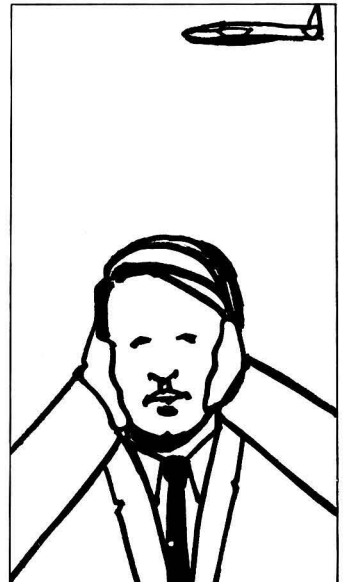- Whether the community has been accustomed to hearing such noises.

Other intangible factors, which our present technology does not enable us to take into account, enter into any predictive scheme for estimating the reaction of a community to noise, including such ones as fear of the noise source itself and economic interest associated with the noise source.

Noisier cities

Are communities becoming noisier each year? The answer undoubtedly is *yes*. But, in point of fact, we do not have a valid objective answer to this question because adequate data have not been obtained. Since the noise level at any selected location in a city varies from moment to moment—with the time of day, with the day of the week, and even from season to season—a considerable amount of statistical information is required to obtain an adequate characterization of the noise at only one location in the city. Similar data are required in a larger number of locations. Yet, because of the practical problems in obtaining such information, sufficient data are not available to indicate how urban environments are changing in noise level.

Community noise control problems

In a noisy community environment, important and, it would seem, obvious methods of noise control often are neglected. The lack of adequate zoning regulations around potential sources of noise complaints often results in serious noise problems. For example, undevel-

oped areas around airports should be zoned so as to exclude specifically land utilization for dwellings.

Another method of noise control—locating a building on a site so as to minimize the disturbing effects of noise—often is overlooked. It is hard to understand why a community will locate the classroom building of a school adjacent to an arterial highway and then place the gymnasium and playing field behind the school building in a quiet area—some distance from the highway—instead of vice versa. This is simply a matter of poor planning.

Many sources of noise pollution in cities are associated with some form of transportation, such as buses, trucks, motorcycles, railroads, aircraft, and automobiles. These sources include acoustic signaling devices, such as horns and sirens, often used unnecessarily.

It is interesting to note that New York City operated hospitals have found that since their ambulances have been forbidden to sound their sirens, they have had fewer accidents, although in case of a dire emergency, a police escort plus siren is provided. It is my opinion that this procedure should be followed in other cities. Ironically, no ordinance has been passed in New York City which prohibits private ambulances from creating a din that sometimes gives a visitor the impression than an air raid warning is being sounded.

It is unfortunate that in many communities irresponsible public servants are the cause of considerable noise pollution. Often, members of the police department sound their sirens unnecessarily. It is not unusual for firemen, returning from an alarm at 3:00 A.M., to roar through a residential area with their sirens wailing and their horns blasting. In these days of reliable two-way radio communication it is questionable whether this quiet-shattering approach is needed.

City-owned garbage trucks often are the principal source of community noise in the early hours of the morning. Perhaps the ordinary citizen would take more seriously existing antinoise ordinances which regulate the noise from boisterous parties, loud radios, high fidelity sets, and window-type air conditioning units if city governments set better examples in avoiding the generation of needless noise pollution. Law enforcement of antinoise ordinances can be effective only if the public supports such measures.

The din of building

Perhaps the major source of noise pollution in many of our cities, other than those related to transportation, are noise sources associated with building construction and street repair—pile drives, jack hammers, compressors, and the like. I am convinced that nothing will be done on a voluntary basis to alleviate the problems that these noise sources create. The only remedy is legislation.

At present, a manufacturer or contractor who is desirous of reducing equipment noise is placed at an economic disadvantage if he installs noise suppression devices, since he must bid in competition against someone else who may not feel that it is important or necessary to spend money for such purposes.

Many responsible people associated

with the construction industry believe that such legislation setting the permissible noise output of equipment must and will come. But the problem is not simple. First, it is necessary to have a standard method of measurement of the noise output of such equipment, then, second, acceptable limits must be established.

There are many practical problems involved in establishing a standard measuring technique that provides a repeatable answer under different field conditions. For example, the measurements must take into account the reflection of sound from nearby buildings. Also, the effects of noise from other nearby sources must be evaluated.

Thus, the first problem in any legislative program is to establish a practical, reliable, and meaningful noise measurement technique for the class of equipment under investigation. After this problem has been resolved, how does one determine what is an acceptable limit for the noise output of a piece of equipment such as an air compressor?

Legislating noise abatement

Opinions differ sharply on how to determine what is an acceptable limit. But here is a method of approach which I believe is practical. For a given class of equipment, we must review data on the noise output of pieces of equipment which have incorporated items of noise control such as silencers, noise shields, sound absorptive materials, and the like. These pieces of equipment would serve as a guide in establishing the acceptable limits. An even lower level may be highly desirable, but this level could be adopted at a later date. Such a step would be only a first step in a legislative program which is realistic in the sense that it could be met by industry.

A different approach would be to set an arbitrary acceptable limit of noise output for a given class of equipment without taking into account the lowest levels that can be attained today. But there is a danger that in so doing one would establish limits which are unrealistically low, in which case the new legislation would probably be ignored.

Privacy in apartments

Another area of possible noise control legislation that could affect city dwellers is that of noise insulation of partitions in multiple-dwelling structures. In a number of European countries, building
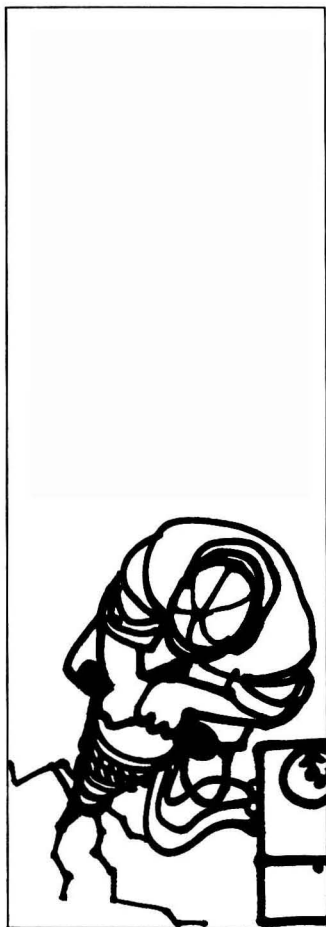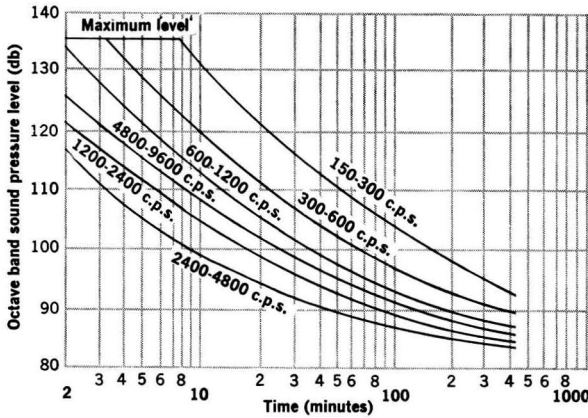
Dangerous effects of noise are related to both pitch and exposure time

"Damage-risk contours" for a single exposure to noise each day. These curves show the sound pressure levels in various octave bands of noise that should not be exceeded. If any single octave band exceeds these limits, daily exposure to the noise can be considered unsafe

Sound-deadening value of partitions varies widely

The sound insulation value of a partition (expressed in terms of the transmission loss in db. vs. the weight per square foot of area of the partition). These empirical data show that the sound insulation value of a homogeneous partition increases 4.4 db. for each doubling of the weight per unit area of the partition
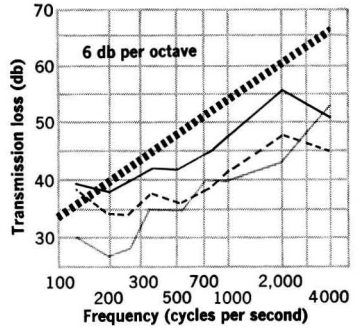
— staggered wood studs with gypsum wall board
- - - hollow gypsum block, plastered
······ steel studs and metal lath, plastered

Certain sounds penetrate partitions easily

Variation of the insulation value of three typical partitions vs. frequency. These data show that the sound insulation value increases about 6 db. for each doubling of frequency
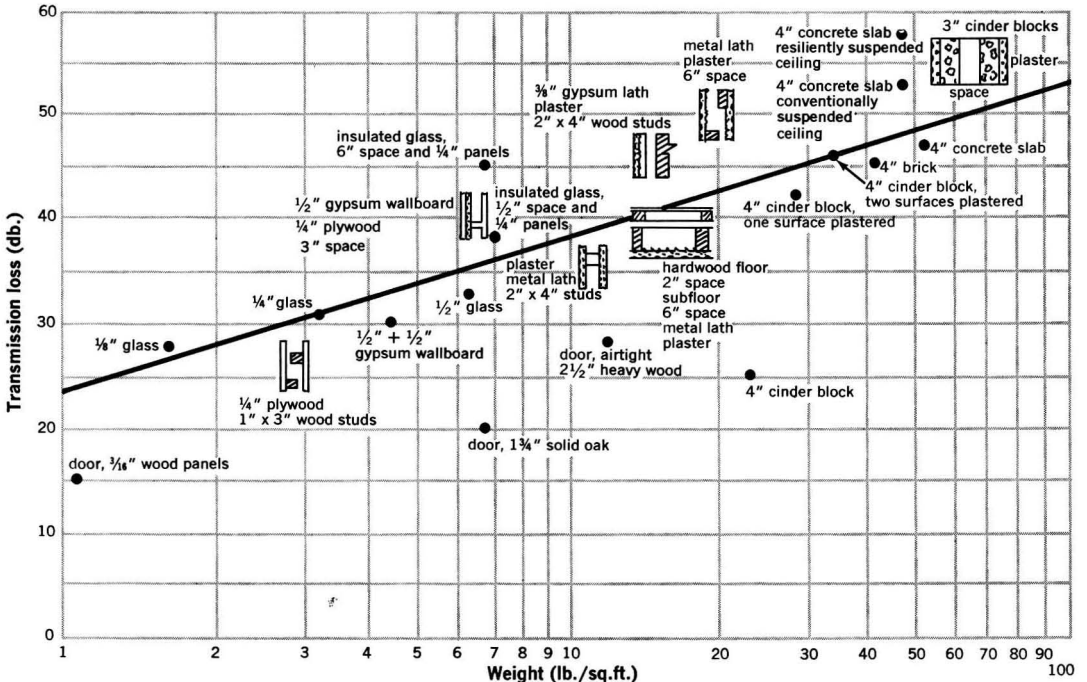
codes specify minimum standards for insulation against airborne sounds and also against impact noises, such as footfalls. However, in this country such legislation is virtually nonexistent.

Why is it that the walls and floors in older apartment houses provide better insulation against airborne sounds than in those built in recent years? The most important factor responsible for poor noise insulation in buildings being erected today is the low mass of the partitions. As a result of low mass, the insulation against airborne sound has been poorer because the noise insulation value of a solid homogeneous partition (such as concrete or brick wall) varies directly with its weight per square foot. The reason for this relationship is that sound waves striking a wall actually provide a sufficient force to set the wall in motion. Although the movement of the wall is minute, it is sufficient to produce noise on the opposite side.

The greater the mass per unit area of a wall, the greater its inertia and the less its movement. Even if a noise source of tremendous acoustic power were to generate noise at a frequency corresponding to that at which the wall is mechanically resonant, the vibration of the wall would be so minute that it is highly improbable that the walls would ever come tumbling down, as was said to be the case at Jericho.

Most sounds of speech and music have frequencies that are much higher than those of the wall's most resonant frequency. Therefore, in theory, the increase in noise insulation should be 6 db. for each doubling of the weight per unit area of the wall. In practice this increase in average insulation value is nearer 4.4 db. per doubling of mass. According to the empirical relationship, which is often referred to as the mass law, a homogeneous partition weighing 10 pounds per square foot has an average noise insulation value of 38 db. If we double the weight per unit area, the noise insulation value increases to 42.4 db.

Most homogeneous walls, regardless of the material of construction, follow this empirical relationship reasonably well. It is well to note, however, that some partitions provide better insulation than the mass law indicates. These are double-wall constructions, or compound wall construction, in which one leaf of the partition is not rigidly connected to the other.

If it were possible to completely iso-late two relatively lightweight walls from one another, the average insulation value for the compound structure would be equal to the sum of the values for each of the walls—in contrast to the 4.4-db. increase if we merely double the weight per unit area of the wall.

In practice, mechanical ties, as well as the entrapped air between the two leaves of a partition, provide a mechanical coupling which reduces the theoretically possible value to a much lower value. But, for a given weight, one can obtain higher noise insulation by using a compound partition than by using a single homogeneous partition.

The data on the noise suppression ability for partitions actually cover noise insulation value averages over all frequencies. However, the insulation of a partition is much greater at high frequencies than at low frequencies, primarily because the wall is a mass-controlled system. That is, noise insulation properties of partitions increase more or less uniformly with frequency, the average increase in insulation per doubling of frequency being about 6 db. It is either relatively poor insulation or low frequency—or both—that accounts for the fact that it is often possible to hear the low frequency booming sounds of your next door neighbor's radio, but not the higher frequency sounds.

Need for noise control

Because a noise-polluted environment has adverse effects on man, it is important that noise control measures be adopted in communities to make them more healthful and more pleasant places in which to work and live. Many of the sources of city noise will be reduced to acceptable limits only if controlled by legislation. Any such antinoise ordinances must be based on field-measurement techniques which are both practical and reliable; and they must set limits which are realistic. In any case, if a noise-abatement program, based upon these ordinances, is to be successful it must have support of the general public.

Suggested additional reading

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Dr. Cyril M. Harris *is professor of electrical engineering and architecture at Columbia University, where he has been on the faculty since 1952. Previously (1945–51), he worked with Bell Telephone Laboratories as a research engineer in acoustics, later (1951–52) spending a year as a visiting lecturer at the Technical University of Delft, Holland and (in 1960) as visiting professor at the University of Tokyo, Japan. He received his B.A. (1938) and M.A. (1940) from the University of California in Los Angeles, and his Ph.D. (1945) in physics from the Massachusetts Institute of Technology. An active acoustical consultant, Dr. Harris is currently involved in such projects as the John F. Kennedy Center for the Performing Arts in Washington, D.C., the Krannert Center for the Performing Arts at the University of Illinois, and the St. Louis Symphony Hall. Dr. Harris is a Fellow of the IEEE and of the Acoustical Society of America, of which he is a past president (1964–65).*

Chemists discuss water resources management

Chemists and chemical engineers have been playing an important role in the control and management of our nation's water resources. Today, their services are in greater demand than ever before as various institutions, governmental bodies, and groups concerned with environmental management seek basic data, concepts, and technologies from which effective control programs can be derived. In an attempt to bring some of these matters together, the ACS Division of Chemical Education and Division of Water, Air, and Waste Chemistry sponsored a joint symposium on water chemistry at the 153rd National Meeting (April 9-14) in Miami Beach, Fla., on the role of chemists and chemical engineers in the study of natural waters, water and waste treatment, and water pollution control. Herewith are condensations of some of the papers, prepared by the authors and obtained with the encouragement and assistance of the symposium chairman, Dr. G. Fred Lee, professor of water chemistry, University of Wisconsin, Madison

1

Chemistry of Water Pollution Control: Discovering the Source and Scope of Chemical Pollution

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Water chemistry is not one of the conventional specialties in chemical education. It is a professional field that is still sparsely staffed. The discerning chemistry student has the opportunity to enter this field and realize a gratifying scientific career that incorporates a rewarding alliance with Nature. One of the specific fields of water chemistry is water pollution control. This is con- cerned with the effects of contaminants on the desirable properties of natural water supplies and how to overcome pollution.

Water pollution control involves every aspect of water chemistry. The reference is unpolluted natural water, which nevertheless contains dissolved minerals, gases, and natural organic matter, as well as many species of living organisms, all in complex relationships. Another aspect of the field is the chemistry of water pollutants. These are roughly classified as municipal wastes and industrial wastes (both organic and inorganic).

Pollutant chemistry deals with: methods of identification and measurement, how pollutants are related to industries and manufacturing processes, where they originate, and their fate when discharged into water supplies. Waste treatment is one of the tools of pollution control. The chemical composition and properties of a waste guide the development of an effective treatment system. Furthermore, success in conscientious treatment is constantly measured by chemical analysis.

Chemistry and pollution abatement

The emphasis in this article is on the effective application of chemistry to abate chemical pollution. Organic chemicals can produce striking pollution effects at concentrations of 1 part per billion or less; they constitute the most challenging chemical pollution problems. There is no routine approach to the analysis of these low concentrations of unknown organics in water.

When a stream pollution incident occurs, the chemist must identify the responsible agents and relate their composition to the kind of stream damage they cause—poisoning of fish, interference with industry, taste and odor in drinking water, or even danger to human life. The source responsible for the pollution is sought by analytical surveillance of waste outfalls and of the polluted stream above and below suspected sources. It is unlikely that there will be assistance and advice from the industries causing pollution or even access to samples within their plants. The chemist must be prepared to carry out his investigation entirely in publicly accessible areas, such as the

polluted bodies of water and their shores.

Having learned the probable identity of the pollutant causing a pollution incident and locating its source in an industrial outfall, the control chemist accumulates further evidence. The intensity and geographic extent of pollution are determined. Possible additional sources of the harmful pollutant are sought. The persistence of the pollutant is determined. These steps are taken to show an unbroken chain of cause and effect between the upstream source and the downstream site of damage. Finally, when the abatement case is proved and corrective treatment is undertaken, the control agency chemist performs analytical surveillance of stream and outfalls to determine whether the treatment actions were effective.

A widely reported—and broadly representative—example of chemistry in water pollution control is offered by the 1963 Mississippi River Fish Kill investigation, to which many scientific specialties contributed importantly. Kills had been observed in the lower Mississippi in Louisiana since 1960, but the ultimate death of many millions of fish in November and December, 1963, brought forth the successful uncovering of the chlorinated insecticide, endrin, as the cause.

Search for causes

At the start of the investigation, biological specialists promptly ruled out a number of suspected causes: abnormal temperature, dissolved oxygen, or pH, disease, parasites, toxic metals, viruses, and botulism. The symptomatology of dying fish and the pathology of dead fish showed distinct characteristics that later confirmed the identification of the responsible chemical. Parallel chemical investigations were begun, with the chemists divided into teams at several laboratories. One team began to study the tissues of poisoned fish. There was evidence that the tissues were toxic to mice. Steam distillates of poisoned fish livers were toxic to the same species of fish, and led to the same symptoms. Another team studied samples of mud from the bottom of the river in the study area. Chloroform extracts of the mud produced the characteristic fish poisoning.

Electron-capture gas chromatography, fortunately, had become available in time for this investigation. Each team

of chemists applied this technique. Four peaks were common to the chromatograms obtained from the mud extract and from all extracts of poisoned fish tissue studied. The two early-eluting peaks were very prominent and for a while were erroneously hypothesized to be the toxic agent. They were later shown to be relatively nontoxic intermediates in the manufacture of endrin.

One team recognized one of the lesser peaks as endrin and supported the identification by gas chromatography on a column that converts endrin into two new characteristic peaks. Each of the four peaks was trapped separately and tested for toxicity. Only the endrin fraction was markedly toxic. Later, a method was developed for the extraction and absolute identification of endrin in tissues of the poisoned fish by infrared spectrometry. The identification of the water pollutant was thus established.

The next step was to show that endrin caused the fish kill. An analysis for endrin in fish blood was developed. It was applied to blood samples of dying fish collected from the Mississippi River and of fish exposed to endrin in the laboratory. In channel catfish, one of the most seriously affected species, it was found that when endrin in the blood reached a concentration of 0.3 microgram per gram through exposure, it was always fatal. When fish were deliberately exposed to nonlethal concentrations of endrin in water, the resulting blood concentrations were clearly lower. But in all the blood samples of dying fish collected from the river, endrin concentrations were so high that death from endrin poisoning was certain.

Although there was little doubt, proof that the river water carried the endrin was obtained. The peak of endrin pollution had passed by the time river samples could be obtained. Some samples, nevertheless, contained endrin in concentrations below but approaching levels toxic to the most sensitive species. Moreover, a striking application of chemical technique came forth at this time.

National program

A national program to monitor organic chemical pollution of the major surface water systems of the country had been pursued for years before this incident. One of the major aspects of the program is the collection of samples of

the gross organic contaminants by adsorption on active carbon. Samples of this type, taken in past years from Mississippi River locations involved in the fish kill, were reexamined and shown to contain endrin, correlating with the fish kills going back to 1960. Thus, an old problem was reexamined by techniques not available when the problem first occurred.

The information detailed above, by similar analyses, led to the discovery of the responsible sources of the endrin pollution. A number were uncovered, but the most striking was an endrin manufacturer who had been discarding tons of waste rich in endrin. All the necessary evidence relating this source with the downstream fish kills was developed, including infrared and nuclear magnetic resonance spectra, resulting in unquestionable proof of the entire cause-and-effect chain. The final act of this drama was a forced cleanup of accumulated wastes, institution of pollution abatement practices, and vigilant monitoring of pesticides in the Mississippi and its tributaries. As a result, the annual cycle of fish kills ended with the one described in this narrative.

Chemistry of Ground Waters: Models for Their Composition

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Natural waters acquire their chemical characteristics by dissolution and by chemical reaction with solids, liquids, and gases with which they have come into contact during the various parts of the hydrological cycle. Terrestrial waters vary in chemical composition; but these variations are, at least partially, understandable if the environmental

history of the water and the chemical behavior of the rock-water-atmosphere systems are considered.

This article attempts to describe, in terms of oversimplified equilibrium models, the chemical behavior of rocks in water. In imaginary experiments individual minerals are added to distilled water and exposed to air containing CO_2. After equilibration, the composition of the water is calculated using equilibrium constants. In establishing these models, we use a variety of elementary principles of physical chemistry—e.g. heterogeneous equilibria describing congruent and incongruent solubility, the phase rule, heterogeneous ion buffering.

The models are inadequate in many respects:

• In real systems, equilibrium may seldom be attained.

• Free energy data on alumino silicates are insufficient in order to define reliable stability relations.

• The exact composition of the mineral phases in the rock are unknown.

Despite these and other limitations, it is expected that equilibrium calculations of the type presented here may in a didactic way illustrate some of the principal regulatory factors that determine the mineral composition of ground waters.
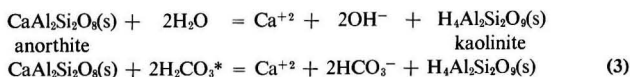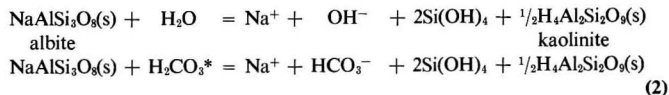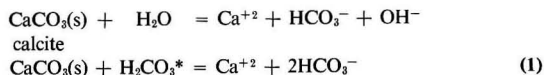
Major dissolved constituents

In a recent survey of the frequency distribution of various constituents in terrestrial waters, Davies and De Wiest have shown that the major dissolved constituents and their median molar concentration (frequency of 50%) are $HCO_3^-(10^{-2.4})$, $Na^+(10^{-2.9})$, Ca^{+2} $(10^{-3.0})$, $Cl^-(10^{-3.2})$, $Mg^{+2}(10^{-3.4})$, $Si(OH)_4(10^{-3.4})$, and $SO_4^{-2}(10^{-3.5})$. Some of the constituents show surprisingly little natural variation in their concentration. For example, 80% of all water analyses for dissolved silica show concentrations between $10^{-3.8}M$ and $10^{-3.2}M$.

In developing our simplified models we do not consider Cl^-, and SO_4^{-2}. These ions are usually not major constituents of igneous rocks and are to a large extent introduced into the water by rainfall. In order not to complicate the systems unduly, we also omit Mg^{+2}. Thus our imaginary experiments yield waters that contain HCO_3^- (CO_2 and CO_3^{-2}), Na^+, Ca^{+2}, and orthosilicic acid, $Si(OH)_4$. Our hypothetical dis-

solution experiments are carried out predominantly with the following minerals: Na-feldspar (albite), $NaAlSi_3O_8$, Ca-feldspar (anorthite), $CaAl_2Si_2O_8$, Na- and Ca-montmorillonite, $Na_{0.33}Al_{2.33}$-$Si_{3.67}O_{10}(OH)_2$, and $Ca_{0.33}Al_{4.67}Si_{7.33}O_{20}$-$(OH)_4$, kaolinite, $H_4Al_2Si_2O_9$.

Dissolution of rocks as acid-base reactions

The dissolution of the minerals may be interpreted in terms of an acid-base interaction: Acids react with the bases of the rocks to form solutions that have pH values within the narrow range from 6.5 to 8.5. Usually, the acid is dissolved CO_2 ($[H_2CO_3^*] = [CO_2] + [H_2CO_3]$). In typical dissolution reactions

$$
\begin{aligned}
CaCO_3(s) + H_2O &= Ca^{+2} + HCO_3^- + OH^- \\
\text{calcite} & \\
CaCO_3(s) + H_2CO_3^* &= Ca^{+2} + 2HCO_3^- \quad (1)
\end{aligned}
$$

$$
\begin{aligned}
NaAlSi_3O_8(s) + H_2O &= Na^+ + OH^- + 2Si(OH)_4 + \tfrac{1}{2}H_4Al_2Si_2O_9(s) \\
\text{albite} & \qquad\qquad\qquad\qquad\qquad\qquad\quad \text{kaolinite} \\
NaAlSi_3O_8(s) + H_2CO_3^* &= Na^+ + HCO_3^- + 2Si(OH)_4 + \tfrac{1}{2}H_4Al_2Si_2O_9(s)
\end{aligned}
$$

$$(2)$$

$$
\begin{aligned}
CaAl_2Si_2O_8(s) + 2H_2O &= Ca^{+2} + 2OH^- + H_4Al_2Si_2O_9(s) \\
\text{anorthite} & \qquad\qquad\qquad\qquad\quad \text{kaolinite} \\
CaAl_2Si_2O_8(s) + 2H_2CO_3^* &= Ca^{+2} + 2HCO_3^- + H_4Al_2Si_2O_9(s) \quad (3)
\end{aligned}
$$

alkalinity is imparted to the dissolved phase from the bases of the minerals. While calcite dissolves congruently, an incongruent dissolution reaction is observed with the feldspars. We speak of incongruent solubility of a salt if the dissolution is accompanied by a phase change. [A well known example is the dissolution of $MgCO_3$. Since the maximum solubility of $Mg(OH)_2$ is smaller than that of $MgCO_3$, addition of $MgCO_3$ to water will lead to precipitation of $Mg(OH)_2$.]

In other words, the weathering reaction, typically, is a hydrolysis reaction; a more acidic solid residue higher in Al than the original silicates is left behind. The dissolution of the feldspars may go over intermediates, not shown in Reactions 2 or 3. Virtually all bonds must be broken in the tetrahedric Al framework structure before rearrangement of the lattice with Al in 6 coordination (as in kaolinite) becomes possible. Understandably, the rate of reaction is very slow; it is accelerated in an acid environment. Table 1 gives a few representative dissolution reactions. It has to be kept in mind that highly schematic and idealized formulas are used to rep-

Table 1. Equilibria considered

Reaction	log k (25° C.)
1) $CO_2(g) + H_2O = H_2CO_3^*$	-1.5
2) $H_2CO_3^* = H^+ + HCO_3^-$	-6.3
3) $HCO_3^- = H^+ + CO_3^{-2}$	-10.3
4) $CaCO_3(s) = Ca^{+2} + CO_3^{-2}$	-8.3
5) $Na\text{-feldspar} + H^+ + \frac{9}{2} H_2O = \frac{1}{2}$ kaolinite $+ 2Si(OH)_4 + Na^+$	-1.9
6) $Na\text{-montmorillonite} + H^+ + \frac{23}{2} H_2O = \frac{7}{2}$ kaolinite $+ 4Si(OH)_4 + Na^+$	-9.1
7) $Ca\text{-feldspar} + 2H^+ + H_2O =$ kaolinite $+ Ca^{+2}$	$+12.4$
8) $Ca\text{-montmorillonite} + 2H^+ + 23H_2O = 7$ kaolinite $+ 8 Si(OH)_4 + Ca^{+2}$	-15.4
9) $Kaolinite + 5H_2O =$ Gibbsite $+ 2Si(OH)_4$	-9.4
10) $SiO_2(\text{amorphous}) + 2H_2O = Si(OH)_4$	-2.7

Stability diagrams help in understanding weathering transformations[a]
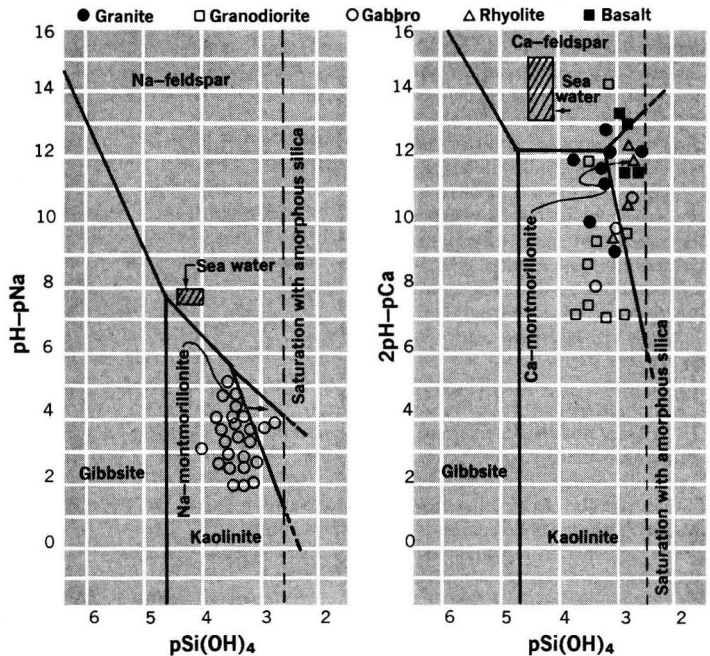
[a] The equilibrium constants given in Table I have been used in the preparation of these diagrams

Table 2. Equilibrium models

Model No.	Components necessary to copy system	Phases	Selected variables (degrees of freedom) in addition to temp.	Equilibrium composition − log concentration (M)					
				H^+	Ca^{+2}	Na^+	HCO_3^-	$Si(OH)_4$	$H_2CO_3^{a}$
1	CO_2, H_2O	$CO_2(g)$; solution	$P_{CO_2} = 10^{-2}$	4.9	...	...	4.9	...	3.0
2	$Ca(OH)_2, CO_2, H_2O$	$CO_2(g)$; solution; calcite	$P_{CO_2} = 10^{-3.5}$	8.4	3.3	...	3.0	...	5.0
3	$NaOH, Al(OH)_3, Si(OH)_4, H_2O, CO_2$	$CO_2(g)$; solution; Na-feldspar, kaolinite	$P_{CO_2} = 10^{-5}$ $[Na^+] = \frac{1}{2}[Si(OH)_4]$	9.1	... ...	3.7	3.7	3.4	6.5
4	$NaOH, Al(OH)_3, Si(OH)_4, H_2O, CO_2$	$CO_2(g)$; solution; Na-montm; kaolinite Na-feldspar	$P_{CO_2} = 10^{-3.5}$	8.35	...	2.95	2.95	3.65	5.0
5	$NaOH, Ca(OH)_2, Al(OH)_3, Si(OH)_4, H_2O, CO_2$	$CO_2(g)$; solution; Na-montm. Ca-montm.[b] kaolinite	$P_{CO_2} = 10^{-2}$ $[Si(OH)_4] = 10^{-3.3}$	7.1	3.2	3.0	2.7	3.3	3.5
6	$NaOH, Ca(OH)_2, Al(OH)_3, Si(OH)_4, H_2O, CO_2$	$CO_2(g)$; solution; Na-montm; Ca-montm.[b] calcite, kaolinite	$P_{CO_2} = 10^{-2}$	7.36	2.9	2.9	2.45	3 4	3.5
			$P_{CO_2} = 10^{-1}$	6.62	2.5	2.8	2.2	3.3	2.5

[a] $[H_2CO_3^*] = ([CO_2] + [H_2CO_3])$.
[b] It may not be appropriate to count Na-montm. and Ca-montm. as two separate phases; if counted as one phase only, the additional condition [Ca-montm.] = [Na-montm.] must be assumed in order to "define" the variables.

resent complex minerals and that in a metaphoric way only a few simple reactions are given to illustrate the very complex weathering transformations.

Stability relations and solubility

With the help of the equilibrium constants given in Table 1, two sets of equilibrium relationships are given in Figure 1. Similar relationships using different constants or different mineral formulas have been given by Feth *et al.* and Garrels and coworkers. Remarkably different predominance diagrams are obtained by choosing different constants and formulas. Such stability diagrams attempt to utilize limited data or even simulated data in order to gain qualitative or at best semiquantitative impressions of a possible actual situation.

In order to better understand the stability relations depicted in Figure 1, we might first consider the equilibrium solubility of individual minerals. The hypothetical systems are made by introducing a mineral into pure water and exposing the solution to a selected partial pressure of CO_2. The concentration of dissolved CO_2 is then determined (Henry's law) by the partial pressure of CO_2:

$$[H_2CO_3^*] = kP_{CO_2} \qquad (4)$$

Congruent solubility of $CaCO_3$ and the phase rule

Under the selected conditions, $CaCO_3$ dissolves congruently. In order to calculate the equilibrium composition the maximum number of unknown concentrations (activities) must equal the number of independent relationships (equilibrium constant, concentration and stoichiometric conditions, electroneutrality). In terms of the Gibbs phase rule, the number of variables, F, that we can choose independently is restricted by the minimum number of components, C, necessary to copy the equilibrium system and the number of phases, P:

$$F = C + 2 - P \qquad (5)$$

In the $CaCO_3$ dissolution system we have P = 3 (calcite, aqueous solution, gas phase). The components are $Ca(OH)_2$–CO_2–H_2O; for example, C = 3. The variables are T, P_{CO_2}, $[Ca^{+2}]$, $[HCO_3^-]$, $[H^+]$, and so on. According to the phase rule, we can assign values to only two variables in order to define the system. For example, by selecting the temperature (that is, equilibrium con-

stants valid at a given temperature) and a partial pressure of CO_2, all other variables—that is, pH, $[HCO_3^-]$, $[Ca^{+2}]$ and so on—are determined. Thus, the calcite solubility system at a given temperature is defined by P_{CO_2}.

The gas composition in soils, usually, is quite different from that in the atmosphere; because of respiration by organisms, the CO_2 composition in soil is up to a few hundred times larger than that in the atmosphere ($P_{CO_2} \simeq 10^{-3.5}$). The composition at equilibrium for $-\log P_{CO_2} = 3.5$ is given in Table 2, and the solubility expressed as $[HCO_3^-]$ is plotted as a function of P_{CO_2} in Figure 2.

Incongruent dissolution of feldspar

Considering Reaction 2, because of the incongruence of the dissolution of feldspar, the number of phases has increased to P = 4 (Na-feldspar, kaolinite, solution, gas), but five components [NaOH, $Al(OH)_3$, $Si(OH)_4$, H_2O, CO_2] are necessary to copy the system. We can select three independent variables, for example T, P_{CO_2} and $[Si(OH)_4]$. Instead of the latter variable, we can (considering that we start out with a "pure" Na-feldspar) specify the stoichiometric relations: $[Na^+]$ or $[HCO_3^-] = \frac{1}{2}[Si(OH)_4]$. Thus, the incongruent equilibrium solubility of feldspar for a mineral alteration can be expressed quantitatively as a function of P_{CO_2} (Table 2, Figure 2). Equilibrium solubility for some minerals is plotted in Figure 2.

According to the phase rule, the addition of each component to an equilibrium system must result in either a new phase or an additional degree of freedom. Thus, if we add to the system already considered Na-montmorillonite, and if this clay coexists in equilibrium with the other two solid phases, only two degrees of freedom (that is, T and P_{CO_2}) remain because the number of components has remained constant. The equilibrium composition (Table 2) can be computed readily.

Fresh water models

In order to obtain aqueous solutions resembling the composition of ground waters, we have to add calcium-bearing minerals. The Ca-feldspar, anorthite, is quite unstable toward attack by CO_2-containing water. As Figures 1 and 2 indicate, Ca-montmorillonite becomes
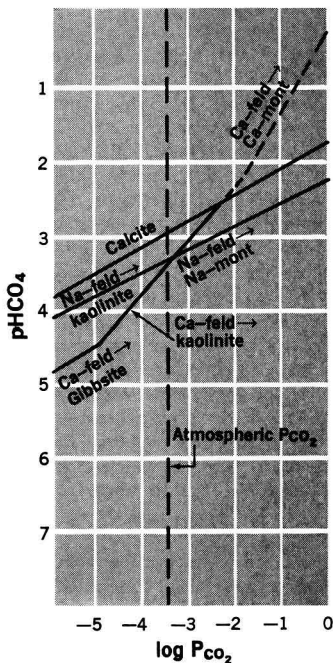
more stable than anorthite at high partial pressure of CO_2 or at high $[Si(OH)_4]$. In model No. 5 (Table 2) kaolinite is assumed to coexist thermodynamically with Ca^{+2}- and Na-montmorillonite. Such a system is still multivariant and in addition to T, P_{CO_2} we have to select an additional variable such as $[Si(OH)_4]$. We obtain an equilibrium composition quite representative of natural fresh waters. At $-\log P_{CO_2} = 2$, the solution is not saturated with respect to calcite. It should be noted that the stoichiometry of the dissolution reactions of calcite and anorthite is identical ($[Ca^{+2}] = \frac{1}{2}[HCO_3^-]$). Therefore a "calcium bicarbonate water" does not necessarily derive from $CaCO_3$. With increased P_{CO_2}, the solution, however, becomes oversaturated with respect to $CaCO_3(s)$. As Figure 2 indicates, the solubility of $CaCO_3$ represents an upper limit for soluble carbonic constituents and calcium.

In Model 6, the coexistence of kaolinite, Na- and Ca-montmorillonite, and

calcite is assumed. The equilibrium composition has been computed for two values of P_{CO_2}. The solution composition for $P_{CO_2} = 10^{-2}$ is very similar to that given for the median composition of terrestrial waters. Water of the type of Model 6 has a nearly constant $[Si(OH)_4]$. The latter concentration varies with $(P_{CO_2})^{1/4}$. Such a hypothetical univariant system shows (as long as equilibrium between all phases is maintained and P_{CO_2} kept constant) an infinite buffer capacity with respect to strong acid or strong base addition (Sillen, Morgan). If this idea is carried a little bit further one can appreciate the working hypothesis, proposed by Sillen, that the ocean represents a coexistence of a sufficient number of phases, so that for the given number of components only one degree of freedom (F = C − P + 2 = 1) remains; then P_{CO_2} in the atmosphere of the model will be determined by the equilibria (especially equilibria among clays) and cannot be varied.

Comparison with real systems

Our models predict that feldspars at the incipiently high CO_2 partial pressures are unstable, with respect to kaolinite. With decreasing CO_2 pressure and sufficient accumulation of $Si(OH)_4$ and Na^+ or Ca^{+2} other clays such as montmorillonite are being formed. If $[Ca^{+2}]$ and $[HCO_3^-]$ become sufficiently large, calcite precipitates and represents an upper limit for the accumulation of soluble ions. Reactions between aluminum silicates are pertinent in regulating the water composition. The predictions of the equilibrium models appear to be in qualitative agreement with many field observations. As demonstrated by Feth et al. $[Si(OH)_4]$ shows little variation with stream discharge. In Figure 1, a few experimental data of analysis of ground waters originating in igneous rocks are depicted. Interestingly, many points fall very close to the montmorillonite-kaolinite boundary.

In presenting simplified equilibrium models, we have tried to abstract from the complexity of nature. For those who are familiar with the complexity of the weathering reactions, the simplification may have gone too far. But it was our intent to reach those who are not students of weathering and to stimulate them to read the excellent papers by Garrels and Mackenzie, Feth, Roberson and Poltzer, Sillen, Holland, Kramer, Hem, and Hemley.

The Chemistry of Rivers and Lakes: The Nature and Properties of Natural Product Organics and Their Role in Metal Ion Transport

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It is generally recognized that the relatively common occurrence of a yellow color in lake water is due to the presence of complex organic matter of natural origin. A reasonably accurate understanding of the environmental factors involved in the production of color or of the significance of this material to the aqueous biological community has been hindered by a lack of significant structural information. In this article I want to question two general theories which have resulted from previous research on the complex natural color system: first, that the molecules producing color are aliphatic in nature; and, second, that their interaction with iron does not involve chelation as a primary mechanism.

The presence of aromaticity is not strikingly apparent from an inspection of spectrophotometric data obtained either on the natural waters or on the organic solids isolated from them. However, we have recently subjected these organic materials to oxidative degradation employing an alkaline CuO system (Christman and Ghassemi, 1966). The degradation products (50% yield) isolated and identified using thin layer chromatography and ultraviolet spectrophotometry are shown in Table 1.

Evaluation of the oxidative system using model compounds has shown that aromatic ring fissure does not occur and that alkyl side chain oxidation occurs only when the alkyl-aryl carbon-

to-carbon linkage is appropriately activated by oxygen-bearing substituents. If the ring is strongly activated, decarboxylation results. Thus it seems justifiable to consider 2,4- and 2,6-dihydroxybenzoic acids as intermediate oxidation products which would be converted to resorcinol during oxidation.

These compounds can be regarded as structural nuclei in the parent macromolecule since it is doubtful they are produced during oxidation and they are definitely not extractable from the untreated colored water. The manner in which these phenolic moieties are bound in the macromolecular structure is unknown. The simplest model one could visualize consists of the aromatic groups bound through extensive alkyl side chain networks. The real structure must be more complicated, probably involving interaromatic linkages, since the foregoing model would demand a chemical reactivity and u.v. absorbance behavior that is not known to exist in real color-water systems. Considering the number and kind of ionogenic groups involved, the ultimate size of any given color-producing structure is probably also a function of pH and total iron concentration.

All of the aromatic substitution patterns shown in Table 1 naturally occur in the extractive fraction of woody tissue and in soil organic matter. Thus, this result is more attractive than the "aliphatic" theory of organic color structure.

One of the most widely recognized properties of organic color is its tendency to associate with iron. Recently, Shapiro (1964) studied this interaction quantitatively and concluded that the organic acids producing color peptize iron in aqueous solution and that this mechanism is more important than chelation.

It is significant that Shapiro also observed the iron-holding capacity of organic color to increase markedly with pH. His theoretical argument, however, included a molecular weight for organic color of 322 and a requirement that aqueous iron be fully coordinated with the color molecule. The magnitude of calculated molar ratios of iron to color seemed to Shapiro to be inconsistent with a chelation model of interaction.

If a molecular weight of 10,000 is assumed (this may be low), a recalculation of Shapiro's data at pH 7.0 reveals

that 100 grams of organic color structure are associated with each mole of iron. This figure is not at all unreasonable for a ligand exchange reaction between aqueous iron and the phenolic units now known to exist in the macromolecular structure of color. Furthermore, it is interesting to consider the following chelation model for color-iron interaction which would show a marked pH dependence.

$$HA \rightleftharpoons H^+ + A^- \quad \text{color ionization}$$
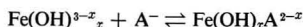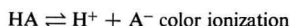
$$Fe(OH)^{3-x}_x + A^- \rightleftharpoons Fe(OH)_xA^{2-x}$$

iron-color chelation

$$[HA] = (A^-) + [Fe(OH)_xA^{2-x}] + (HA)$$

$$[Fe] = [Fe(OH)^{3-x}_x] + [Fe(OH)_xA^{2-x}]$$

where brackets indicate total concentrations and parentheses indicate equilibrium concentrations.

Combining the equilibrium constant expressions for the ionization (K_a) and chelation (K_c) reactions leads to:

$$\kappa = K_a K_c = \frac{(H^+)[Fe(OH)_xA^{2-x}]}{(HA)[Fe(OH)^{3-x}_x]}$$

Substituting for total concentrations where possible and rearranging:

$$\log \kappa = \log \frac{[HA] - (A^-) - (HA)}{(HA)} +$$

$$\log \frac{(H^+)}{[Fe] - [HA] + (A^-) + (HA)}$$

If it is now assumed that HA is a very weak acid $[(A^-) \ll (HA)]$ and that the chelation is strong $\{(HA) \ll [HA]\}$, the expression becomes:

$$\log \frac{1}{[Fe] - [HA]} =$$

$$pH \left(1 - \frac{1}{pH} \log N\right) + \log \kappa$$

where $N = [HA]/(HA)$.

The reason I have arranged this expression in the above manner is simply because the quantities [Fe], [HA], and pH are essentially the experimental quantities reported by Shapiro. Thus this chelation model predicts a straight line relationship between $\log 1/([Fe] - [HA])$ and pH, with an intercept of $\log \kappa$. When the reported quantitative interaction data are plotted with this relation a perfect straight line results and a κ value of approximately 10^5 is obtained.

There are of course many questionable assumptions involved in this model, but the result indicates the point I wish to make, namely that the existing data on color-iron interaction are not inconsistent with a chelation mechanism.

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Shapiro, J., "Effect of Yellow Organic Acids on Iron and Other Metals in Water," *J. Amer. Water Works Assoc.*, **58** (8), 1062 (1964).

4

Chemistry of the Oceans: Some Trace Metal-Organic Associations and Chemical Parameter Differences in Top One Meter of Surface

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The impact of the present surge of interest in oceanography on chemistry of the oceans will doubtless be far reaching. In the past few years, chemistry has grown from a one- or two-man operation, mostly of analytical type, at each oceanographic institute or department to a group of fundamentally trained scientists attacking broad chemical problems of the oceans.

As is usually the case, the recent advances have been preceded by new chemical concepts and techniques. The long-awaited utilization of instrumental methods for a much refined analysis of the major component relationships, such as salinity, have greatly enlarged our ability to detect minute differences in water properties. Perhaps the greatest advances, however, have occurred in the minor component and trace element areas. Development of such sensitive procedures as neutron activation analysis, radioactive detectors, isotopic dilution, polarography, mass spectrometry, gas chromatography, atomic absorption spectrometry, and thin layer, paper, and column chromatography has

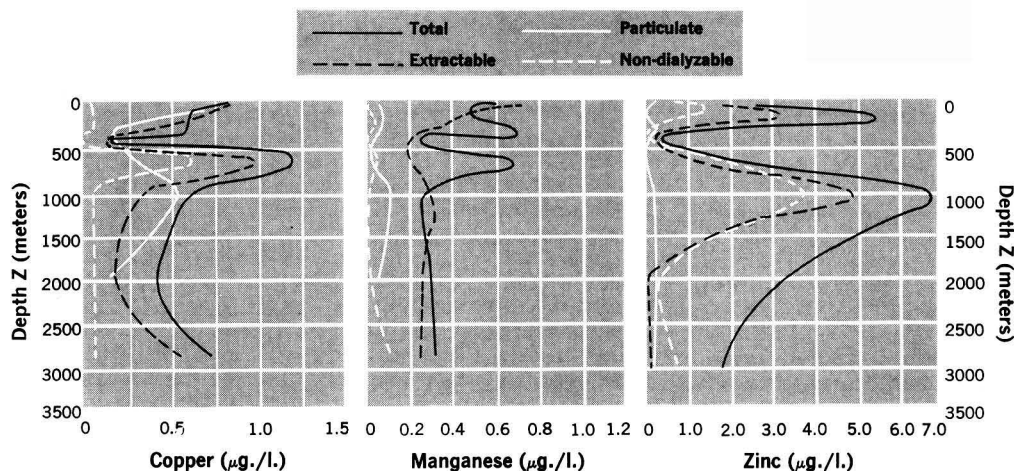Table 1. **Degradation products of natural organic color**

Compound	R_f, in solvent[a]			Absorption maxima, mμ	
	1	2	3	EtOH	EtOH–NaOH
O-Dihydroxybenzene	0.96	0.41	0.55	203, 219, 279	262, 290
M-Dihydroxybenzene	0.98	0.31	0.48	205, 223, 277, 283	245, 295
3-Methoxy-4-hydroxy-benzaldehyde	0.89	0.59	0.68	210, 255, 320	250, 350
3-Methoxy-4-hydroxy-benzoic acid	0.26	0.10	0.57	259, 293	300
3,5-Dimethoxy-4-hydroxybenzoic acid	0.03	0.03	0.51	213, 272	303
3,4-Dihydroxybenzoic acid	0.37	0.05	0.29	208, 252, 292	277, 302
3,5-Dihydroxybenzoic acid	0.20	0.00	0.24	. . .	. . .

[a] Solvent 1: ethyl ether.
Solvent 2: benzene and ethanol (90:10) v./v.
Solvent 3: benzene, methanol, and acetic acid (95:8:4) v./v.

Distribution of chemical and physical forms of copper, manganese, and zinc shows wide variation in ocean waters[a]

Legend: Total, Particulate, Extractable, Non-dialyzable

Copper (µg./l.) — Manganese (µg./l.) — Zinc (µg./l.)

Depth Z (meters)

[a]Data taken at Station 63A1-3 (25° 30'N; 93° 50'W) in Sigsbee Deep, Gulf of Mexico (from Slowey, 1964)

Table 1. Cu, Mn, and Zn according to physical size in the ocean (open ocean, Gulf of Mexico)

Physical	Trace metal content
0.45μ	Mostly Cu (substantial amounts), some Zn, negligible Mn
$0.01-0.45\mu$	Mostly Cu, occasional Zn, negligible Mn
$0.002-0.01\mu$	Mostly Zn (substantial amounts), some Cu, negligible Mn
0.002μ	Mn (almost all), substantial amounts of Cu and Zn

Table 2. Statistical analysis of dissolved organic carbon (D.O.C.) and nutrient concentrations in water collected from the surface and from 1 meter

Nutrient	No. of paired observations[a]	Mean difference[b]	Calculated "Students's" t
D.O.C.	66	+0.44	3.62[c]
$PO_4^{-3} - P$	71	+0.080	3.67[c]
$NH_4^+ - N$	60	+0.311	4.39[c]
$NO_2^- - N$	68	+0.0084	2.42[d]
$SiO_4^- - Si_4$	68	+0.723	1.19

[a] Degrees of freedom, $n - 1$.
[b] Mean difference expressed in µg. A./liter except for D.O.C. which is mg./liter.
[c] Significant at the 0.1 % level.
[d] Significant at the 5 % level.

Goering and Menzel (1965).

provided means not only to estimate total quantities, but to resolve the dynamics of chemical cycling and contributing chemical forms in the system.

Trace element chemistry, as recently elucidated, especially by neutron activation analysis and associated techniques, points to a complexity of chemical forms with elemental specificity. Many elements are found associated with particulate matter of various sizes while others of similar chemical properties may be found wholly in the dissolved state. Recent data obtained by Slowey and Hood (1964) shown in Table 1 demonstrate this point for Cu, Mn, and Zn. Arbitrarily, we chose 0.01μ and less to be in true solution and sizes greater than this to be particulate matter. The fraction 0.002μ was obtained by ultrafiltration through viscose dialysis tubing. The portion retained, commonly called nondialyzable, is attributed to organic complexes firmly bound in the sea water. Other studies showed the divalent forms of the elements dissolved in sea water as assessed with Mn^{54}, Cu^{63}, and Zn^{65} radioisotopic tracers to be extractable with diethyldithiocarbamate and completely removed by dialysis. The nondialyzable portion upon oxidation with

persulfuric acid, a method used for analysis for the total element present, was extractable with this reagent. The distribution of all fractions of Mn, Cu, and Zn investigated, in a column of water in the Sigsbee Deep, is shown in Figure 1.

This figure demonstrates the marked vertical variation in kinds and amounts of these trace metals in the ocean. Likewise, horizontal variability, particularly in surface waters, is also great.

The problem of types of organic compounds associated with the trace metals is almost untouched. Some data from iron exist and recently Slowey *et al.* (1964) isolated a fraction of the Cu in some sea water samples with chloroform and showed it to be associated with phospholipid, porphorin, or aminolipid components.

The organic chemistry of sea water has drawn considerable attention in very recent years. Methods of isolating dissolved organic material in sea water and of characterizing its rapidly proliferating constituents open up new ways of understanding biological and geochemical cycles in the sea and some important aspects of air-sea interactions. Sea surface chemistry with particular reference to the top 1 meter has resulted in some exciting observations. Goering and Menzel (1965) and Goering and Wallen (1966) showed highly significant differences in the concentration of dissolved organic carbon, HPO_4^-, NH_4^+, and NO_3^- at the surface and at 1-meter depth as shown in Table 2. These data are the first to show chemical parameter anomalies near the very important sea-air interface, which may be important in mass transfer and heat and momentum exchange phenomena.

Recent analysis of sea water for He, Ne, Ar, Kr, and Xe by mass spectrometric techniques has revealed excess He over the noble gases in the deep ocean. This excess has been attributed to an influx of atoms of this gas from the lithosphere, where it is produced by natural radioactive decay of members of the uranium and thorium series. If steady state is assumed the rate of He escape from the earth can be computed. Rare gases may also be used for studying the mixing of water masses in the deep ocean, since the concentration in sea water is determined by the equilibrium with the atmosphere when the water is at the surface.

Suggested additional reading

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Goering, John J., and Wallen, David, *Deep-Sea Res.*, **13,** 777 (1966).
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5

The Analytical Chemistry of Water and Waste Waters

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Chemical analysis for pollution control. The seriousness of the problem of water pollution and its impact on environmental health are presently the focus of national attention. Never was there a time in the history of man when he was so deeply concerned with the quality of his water. The analytical chemist, as a member of a team combining various professionals such as scientists, engineers, lawyers, sociologists, physicians, and economists, plays a significant role in the total effort of water pollution control. His role requires him to characterize the nature and magnitude of the problem, assist in executing a control measure or treatment process, and last but not least, provide continuous surveillance and monitoring of the final product—that is, clean water. To this effect the analytical chemist is the "eyes" and "ears" of any control measure, for without valid, meaningful analysis our efforts to control pollution will be fruitless.

There was a time when all that water analysts did consisted of simple titrimetric and gravimetric procedures. Nowadays, with the obvious increase in the magnitude and the ways in which man is polluting his waters, there is an ever broadening need for more accurate and precise information on water quality. The determination of a specific element or compound in a water sample frequently requires extensive separation work to remove interfering constituents before identification and quantitative measurements can be performed. All too frequently, this is followed by one or multiple identification procedures which may involve the use of such sophisticated instruments as emission and absorption spectrometry, mass spectroscopy, NMR, x-ray, thermochemical, and electrochemical techniques. For example, the analysis for certain organic compounds in river waters requires, at first, concentration by adsorption on carbon columns, or partial freezing or reverse osmosis membrane techniques. This is followed by separation with liquid-liquid extraction, gas-liquid chromatography, or thin-layer chromatographic techniques and, finally, identification and measurement by infrared spectrophotometry.

What is unique about water analysis? The chemical analysis of natural and waste waters is one of the most challenging tasks that is likely to confront any analytical chemist. The test solution is, in most cases, a complicated heterogeneous system that rarely lends itself to simple analytical techniques. "Water" analysis requires the subtle correlation of theory and experience of analytical principles, insight into the nature of interferences and other problems associated with the methodology, and the ability to properly interpret analytical results in correlation with pertinent field observations and the history of the water.

Water pollution control can be looked at as a specialized technology and, like any other industry, it has its own specific analytical needs. Analysis may be required to:

• Determine the compliance of certain waters or waste waters to quality standards for an intended use, production control, or disposal in a receiving stream.
• Estimate the possible detrimental effects of waste effluents on the quality of a receiving water for subsequent downstream use.
• Evaluate treatment requirements in view of water reuse.

Some of the more unique analytical parameters characteristic of the water pollution control industry are the BOD (biochemical oxygen demand), COD (chemical oxygen demand), odor, taste, color, chlorine demand, hardness, alkalinity, bioassay using fish or Crustacea, and biodegradability tests. The analytical chemist experienced in water quality characterization can decide, based on practical intuition, what parameter and test to use for a given purpose of analysis.

Selection of methods of analysis is usually based on familiarity with the purpose of analysis; required speed, frequency, accuracy, and precision; effect of interferences; effect of systematic and environmental conditions on sampling and measurements; and collection, transportation, and storage of samples. Screening tests are often used to approximate required sample volumes, establishing desirable sites and frequency of sampling, and to provide a rough estimate of the water composition.

Perhaps the most challenging and most meaningful type of analysis for water quality characterization is that which involves *in situ* measurements. This technique is preferred over analytical procedures which involve removal of the water from its natural environment, in the form of "grab" samples or in the form of a continuous flowing stream, for the subsequent analysis in the laboratory or field station.

Certain parameters easily lend themselves to *in situ* measurements such as temperature, turbidity, pH, and salinity. Electrochemical techniques, in general, are suited for *in situ* measurements. The effect of interferences, due to the presence of electroactive as well as surface active species in the test solution, can be minimized by covering the indicator electrode with perm-selective membranes. Examples of such systems are the voltammetric membrane electrode systems used for the *in situ* measurements for dissolved oxygen (Mancy, Okun, and Reilley, 1962) or certain metal ions (Bowers *et al.*, 1961). Potentiometric membrane electrode systems using glass or crystal membranes have been also used for measurements of specific cations and anions (Bowers *et al.*, 1961; Rechnitz, Kresz, and Zamochnick, 1966).

What are the responsibilities of the water analyst? In the water pollution control field the analytical chemist is expected not just to prescribe a workable procedure, but also he is asked to optimize the technique in order to reduce the time and effort required to obtain the needed information. Besides his responsibility for chemical analysis, a good part of his effort is devoted to diagnosis of problems, definition of analytical needs, design of measurement systems, and development of a master plan of how to report, evaluate, and integrate information with that of other efforts on the same problem.

Why is there a lack of manpower? In line with the general manpower shortage of analytical chemists in all phases of industry, pollution control suffers from a severe lack of qualified analysts. There are several reasons for this problem. In the first place, at a time when the demand for qualified analytical chemists is higher than ever before, formal analytical chemistry courses are, strangely enough, disappearing from undergraduate chemistry curricula.

More exasperating is the fact that little emphasis is given in the majority of water chemistry and environmental sciences graduate programs to water analysis per se. Education in water analysis is presently fragmented into other courses dealing with chemistry of water and waste water. Some educators in water chemistry feel that when it comes to chemical analysis, it is appropriate to send the student to take a graduate course in analytical chemistry rather than undertaking a one-semester course for the analysis of water and waste water. In my opinion, this is expedient, but not necessarily appropriate. This philosophy, in essence, claims that if the applied scientist is taught the fundamentals, he is capable of deducing the applications himself. This may be true, but it is indeed a very slow, expensive process and for a new graduate, it may take him years to "deduce" these applications. If we believe in the merit of experience, then it is more appropriate to teach this factual information directly.

In an era dominated by specialization, it seems that the most capable analytical chemist is the one who is best informed on the applicability and limitations of his techniques in a given job. This should not be done, however, in replacement of principles of analytical chemistry which are considered basic requirements in the background of any analytical chemist.

The seeming lack of opportunity or the nonattractiveness of the water pollution control field to analytical chemists should be blamed, in part, on the managers and directors of the programs. There is an apparent apathy on the part of some directors to give the analytical chemist more responsibilities on the managerial level. This stems from their belief that chemical analysis is nothing but a supporting function to the main effort and responsible, decision-making positions should be occupied by engineers or physicians. This is in contrast to the recognition earned by analytical chemists in academic and various industrial fields. The opportunities for growth and advancement of an analytical chemist should be limited only by his ability, initiative, efforts, and the judgment he exercises.
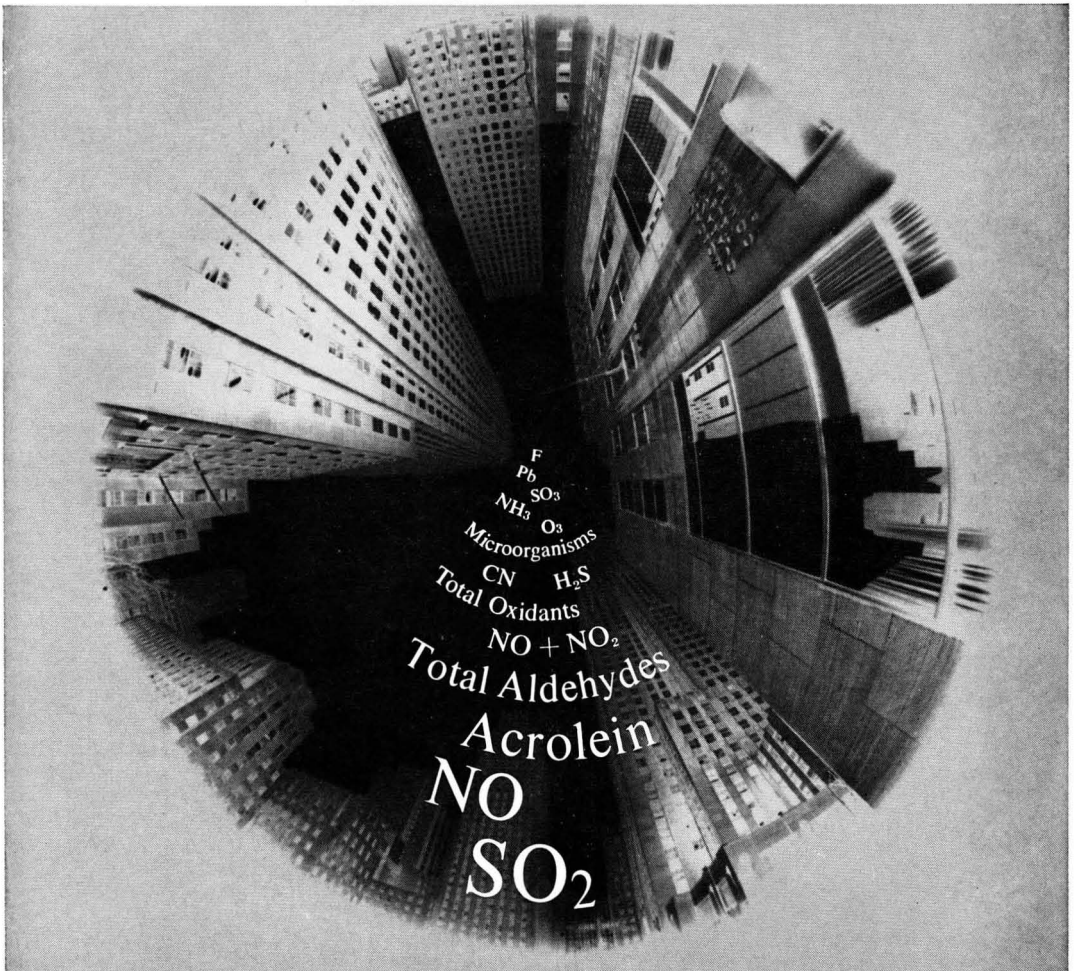
On the national level, our American Chemical Society should take a more active role in educating the public to the problems of environmental pollution. The problem of pollution is everybody's concern. As Dr. Laitinen (1966) says in his editorial: "A scientist properly shows loyalty to his own specialty in discussions within his own branch of science. But the dimensions of his loyalty expand as the boundaries of the discussion become broader. Analytical chemists, for example, might engage in a lively dispute about the relative merits of polarography or gas chromatography in the solution of a particular problem; but their differences rapidly disappear when discussion involves the validity of the analytical approach, as compared to some other approach to the problem. What is more important, however, analytical chemists as well as other specialists should demonstrate their loyalty to chemistry as a whole, and not to one branch of it, when discussing problems of interest to the whole chemical science."

Suggested additional reading

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

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CURRENT RESEARCH
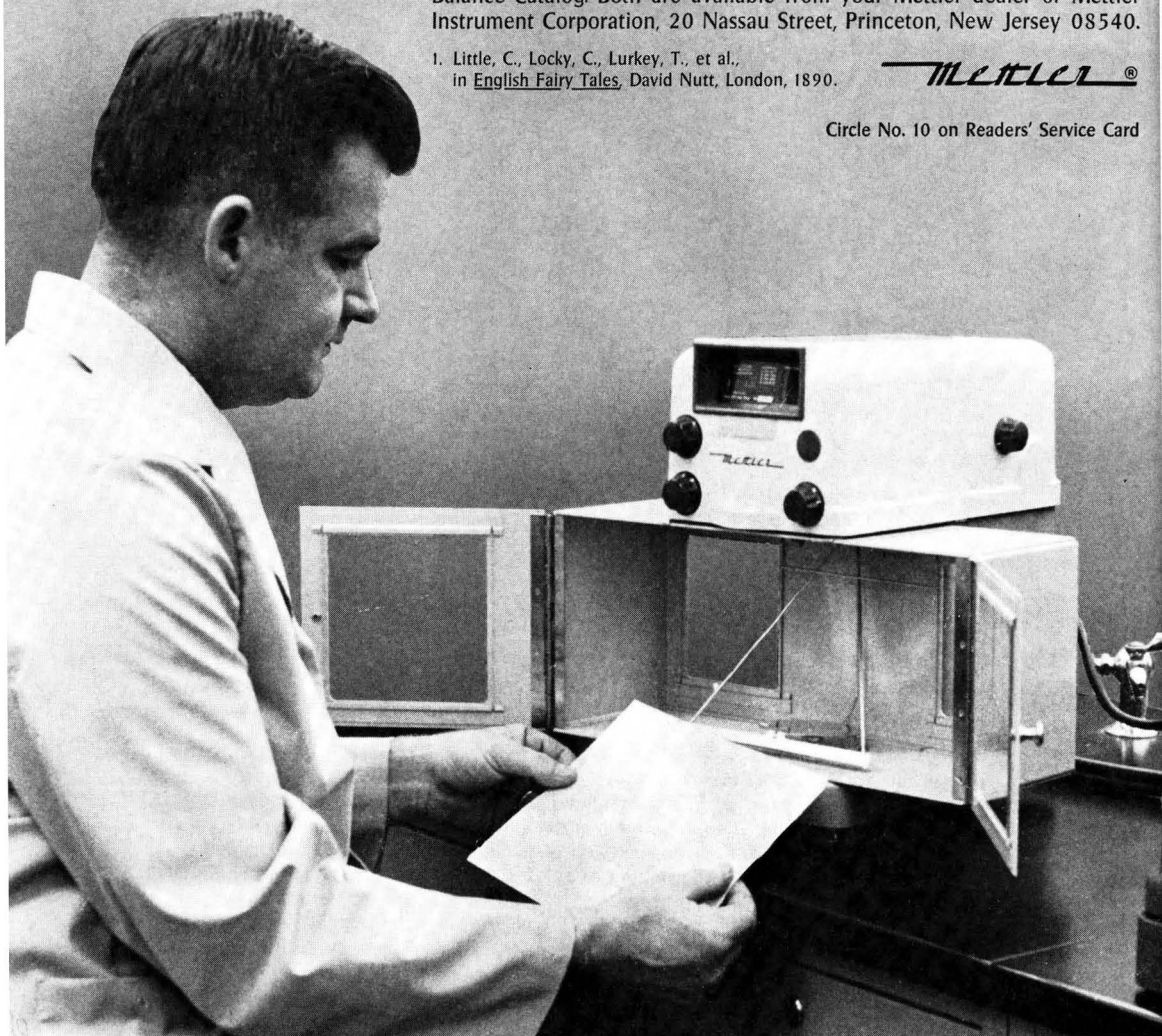
Application of Subtractive Techniques to the Analysis of Automotive Exhaust

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Bureau of Disease Prevention and Environmental Control, U.S. Department of Health, Education, and Welfare, Public Health Service, National Center for Air Pollution Control, Cincinnati, Ohio 45226

■ A simple system, developed for chemical class analysis of hydrocarbons found in automotive exhaust should prove useful for evaluating the contributions of automotive emissions to photochemical air pollution. The system of scrubbers permits determination of paraffins, olefins and acetylenes, and aromatics. Benzene may be determined with either the paraffinic or aromatic hydrocarbons. The system may be used with existing standard hydrocarbon analyzers without requiring their modification.

As devices to control automotive emissions are installed and operated, a simple method of assessing the pollution potential or "smog" potential of the emissions may be required. A complete, detailed chemical analysis of automotive emissions entails large investments in equipment, time, and technically trained personnel. Evaluating the resulting mass of data also requires more effort and expense than are justified for certain basic surveys or studies. To be useful, an analytical method for such applications should be simple enough to be performed by persons without extensive training in chemical analysis. Initial costs should be low, and maintenance requirements minimal.

One approach to such a simple analytical method is to adapt existing hydrocarbon analyzers so that the resulting system analyzes classes of compounds in groups according to their reactivity in the atmosphere. Although our knowledge of the smog potential of various compounds is incomplete, considerable work has been reported that delineates the important classes of compounds. Most investigators would agree that the one- through three-carbon paraffins, benzene, and acetylen eare of negligible reactivity. The four-carbon and higher molecular weight paraffins have very low reactivity. All aromatics except benzene are reactive, as are all olefins.

In the method described here, samples of dilute automobile exhaust are passed through a system of scrubbers to remove components selectively. One column removes olefins, and another removes olefins and aromatics except benzene. By subtraction from the total, the hydrocarbons are reported according to reactivity class. The scrubber system is external to the analyzer, and no modification of the instrument is required. The prototype system, shown in Figures 1 and 2,

was constructed at a cost of about \$300 for parts. The scrubbers were fabricated from readily available chemicals. Several sources of chemicals were used, and all were satisfactory. The analysis is repetitive, and results may be displayed on a recorder, as shown in Figure 3.

A Beckman flame ionization analyzer Model 109 was used in this work. An automatic cycling timer (Crammer Controls, Inc.) was incorporated to regulate the several components of the analysis. This timer operates solenoid valves that divert the sample flow through a single scrubbing system, while the scrubbers not in use are maintained in a "backflush" condition to purge any incompletely absorbed materials. Stainless steel solenoids were selected to reduce possible corrosion problems.

Similar techniques have been used in other applications. Innes *et al.* (1963), Seizinger (1964), and others have described the use of scrubbers in hydrocarbon analysis; Smith and Ohlson (1962) have described the use of similar materials in chromatographic columns. This laboratory (Bellar *et al.*, 1964) has used silver nitrate–ethylene glycol to separate paraffins and olefins in regular chromatographic analysis. Others (Mayrsohn and O'Neal, 1964; Mills *et al.*, 1948; Ryke *et al.*, 1947; Watt *et al.*, 1954; Watt and Walling, 1955) have used similar materials in somewhat different applications with similar results.

Experimental

Initial efforts to produce scrubbers with satisfactory life expectancy showed that ethylene was the most difficult reactive material to remove. A wide range of possible metal salts were surveyed primarily for their ability to retain ethylene. Only the salts which showed considerable retention of ethylene were studied further.

The most promising materials were the salts of silver, mercury, palladium, and platinum. Preliminary checks showed that these salts removed 90 to 100% of the ethylene and less than 5% of a variety of paraffins.

For the convenience in handling, supported solutions were investigated. These may be packed into tubes in the laboratory and shipped to the point of use. The tubes may then be used as the scrubbing tubes in the sampling system without direct handling of reagents by operating personnel. The efficiency of these supported absorbents is equal to that of the solutions,
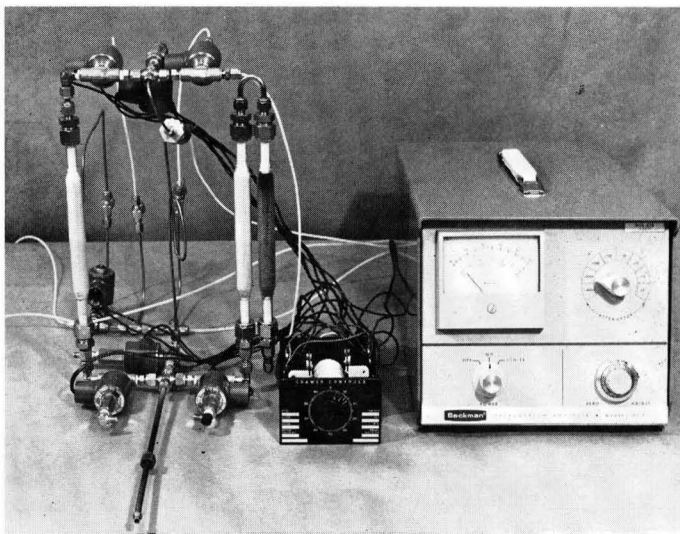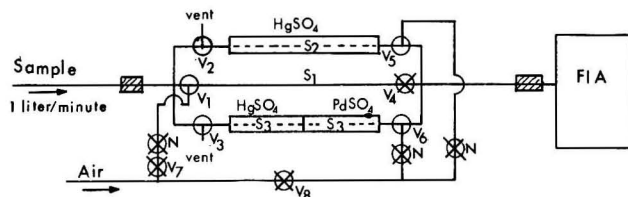
Figure 1. Scrubber system

Figure 2. Flow schematic of subtractive analyzer system

		Cycle					
Posi-tion	Sample Seen by FIA	Flow Path	Scrubber	Valve $V_{1,7}$	Operation of Valves $V_{2,5}$	$V_{3,6}$	V_4
1	Air	S_1	None	On	Off	Off	On
2	Paraffins and benzene	S_3	HgSO$_4$ and Pd	Off	Off	On	Off
3	Total olefins	S_2	HgSO$_4$	Off	On	Off	Off
4	Total	S_1	None	Off	Off	Off	On

Table I. Efficiencies of Supported Absorbents

Material	Acid	Support	Efficiency, % of Compound Removed Ethylene	Aromatics	Paraffins
		Firebrick	0		
20% HgSO$_4$	20% H$_2$SO$_4$	Firebrick	95	0	0
30% HgSO$_4$	20% H$_2$SO$_4$	Glass fiber	0		
0.5% phenol					
Carbowax 400	H$_2$SO$_4$	Firebrick	High background (200 p.p.m. C)		
AgNO$_3$					
MnO$_2$					
CuSO$_4$	H$_2$SO$_4$	Firebrick		0	
AuCl$_2$	H$_2$SO$_4$	Firebrick	50–60		
PdSO$_4$	H$_2$SO$_4$	Alumina	99	99	0
25% AgSO$_4$	50% H$_2$SO$_4$	Firebrick	100		
Pt(SO$_4$)$_2$	H$_2$SO$_4$	Firebrick	15	25–100	0
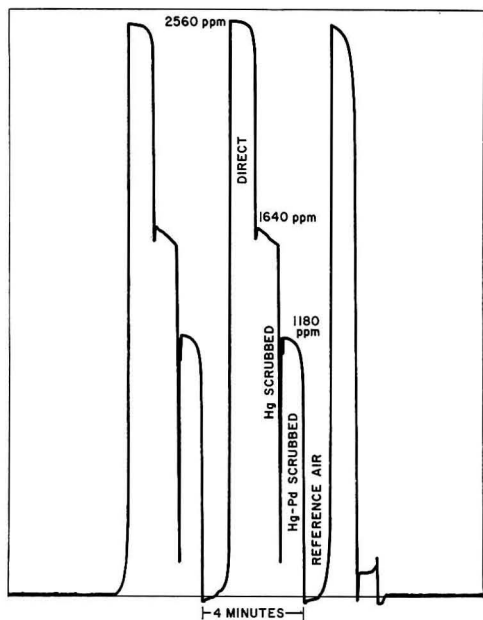
Figure 3. Diluted auto exhaust as seen on flame ionization analyzer with subtractive system

2560 ppm

DIRECT

1640 ppm

1180 ppm

Hg SCRUBBED

Hg-Pd SCRUBBED

REFERENCE AIR

├─4 MINUTES─┤

although the useful life of the individual scrubber is reduced because of the smaller amount of active reagent present.

It is desired to scrub the total sample presented to the instrument to eliminate the need for physically modifying the analyzer. Use of very finely divided firebrick (60- to 80-mesh) restricted the sample enough to cause a change in instrument response. Use of 30 -to 40-mesh firebrick, or Chromosorb W, reduced the sample flow rate 1% or less and caused no apparent change in pressure or instrument response.

Surveys of supported materials are summarized in Table I. The addition of Carbowax 400 to the supports led to high backgrounds.

Mercury Sulfate–Sulfuric Acid. Olefins and acetylenes were efficiently removed by a mercury sulfate–sulfuric acid scrubber. This scrubber was prepared as reported by Innes *et al.* (1963) but with twice as much mercury sulfate. A saturated solution was prepared by dissolving 40% by weight $HgSO_4$ in 20% by weight H_2SO_4 in water. One milliliter of this solution per gram of firebrick was thoroughly blended together. After the mixture dried, an additional 0.5 ml. per gram was thoroughly blended into the coated firebrick.

With approximately 20 grams of packing the differences in useful life between scrubbers prepared with 20 and 40% $HgSO_4$, with and without backflush, can be seen in Figure 4. These scrubbers were used for over 300 1-minute samples of raw automotive exhaust diluted 3 to 1 in nitrogen.

As the scrubber is used, the packing becomes yellow, and its condition can be evaluated easily. Scrubbing efficiency is reduced if the scrubber is allowed to become too dry, a condition first evidenced by a change in texture and later by blackening of the scrubber. Drying may be caused by excessive

Table II. Effect of Water on PdSO₄ Scrubbers[a]

Water, %	Pd, %	No. of Samples Through before Evaluation	Evaluation
7	2		Toluene breakthrough
5	2	1	Toluene breakthrough
5	2	No HgSO₄ prescrubber	Ethylene breakthrough
2	2	270	Toluene removed, benzene through
2	2	400	Acetylene breakthrough
2	4		Benzene partially scrubbed
2.5	2		Toluene removed, benzene 80% through
1	2	10	60% benzene removed

[a] HgSO₄ prescrubber used except as noted.

backflushing with dry air or nitrogen. The scrubbers should be replaced when this condition is noted.

The scrubbers may be regenerated by heating the packing in an open crucible until SO_2 fumes cease to be evolved. After the packing has cooled, 1.5 ml. of 20% H_2SO_4 per gram of material is blended in and the scrubber is repacked.

Palladium (Sulfate–Sulfuric Acid). Palladium salts showed low efficiency for removal of benzene while apparently maintaining efficiency for the removal of higher aromatic hydrocarbons. This substrate was investigated in detail.

The palladium-containing system is not as efficient for scrubbing olefins as the mercuric sulfate–sulfuric acid system. Acetylene broke through the palladium scrubber very quickly and was closely followed by ethylene. Since these compounds are extremely abundant in automobile exhaust, a mercury sulfate–sulfuric acid prescrubber was used to remove the acetylene and ethylene. This prescrubber is a separate mercury sulfate–sulfuric acid scrubber, not that used in the olefin analysis.

The work with palladium is summarized in Table II. The water content of the system is critical. If the concentration of water is kept close to 2% and that of the palladium at 2%, approximately 80% of the benzene will elute, while the toluene is effectively retarded. Efficiencies for toluene range from 95 to 100%. As the system becomes drier, more of the benzene is removed.

The most effective palladium scrubber is prepared by blending 2% by weight palladium chloride dissolved in 10% HCl with 98% 30- to 40-mesh firebrick. This mixture is then heated until HCl fumes cease to evolve. After the mixture cools, 10 ml. of a 2% solution of H_2O in concentrated H_2SO_4 is blended with each 15 grams of the coated firebrick.

Approximately 20 grams of material was packed in $^1/_2$-inch glass tubes. Their condition may be checked conveniently, since the palladium turns from brown to black as aromatics are removed. The scrubber is usually replaced after the black color is approximately halfway down the tube. Excessive drying of the scrubber is also obvious, since the material changes to a lighter brown and looks dry.

Two separately prepared palladium scrubbers were life-tested by comparing the concentrations of automobile exhaust diluted to approximately 3000 p.p.m. of carbon in dry

Figure 4. Ethylene scrubbing efficiency of HgSO₄–H₂SO₄
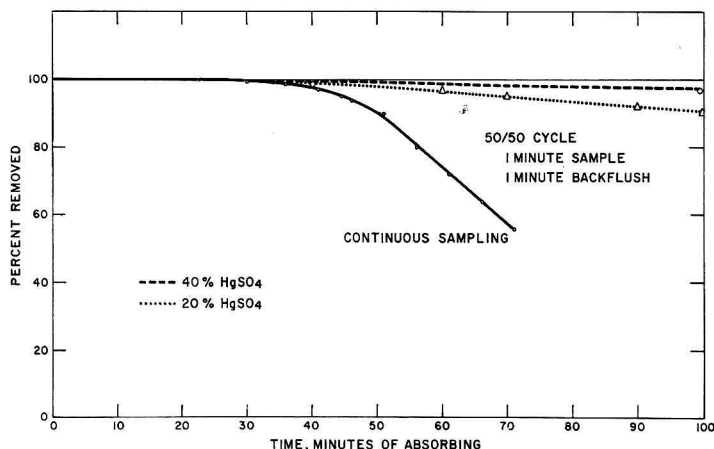
nitrogen after scrubbing for successive cycles. The cycle consisted of 1 minute to the FIA and 1 minute backflush. After 300 cycles the amount removed by the scrubber decreased by 1%.

These scrubbers can be regenerated by heating the packing with mixing over a burner until fumes cease to be evolved and then adding 10 ml. of the 98% H_2SO_4 and 2% H_2O solution per 15 grams of packing. After the material is blended thoroughly, its service life is similar to that of newly prepared material. Several batches have been regenerated six times with no apparent losses in efficiency.

Other Materials Investigated. Evaluations of the salts which appeared to have utility are shown in Table III. In addition to the salts of mercury and palladium already mentioned, two other salts were surveyed in some detail. The platinum salts showed no particular advantages and were abandoned early.

Silver sulfate scrubbers were prepared by dissolving 20 grams of silver sulfate in 10 ml. of concentrated hot sulfuric acid and blending with 20 grams of firebrick. The silver scrubber efficiently removed both olefins and aromatics. Tests of this scrubber showed 99% scrubbing efficiency for 100 1-minute samples with backflush. This system removes all aromatics, including benzene. Since benzene is considered nonreactive, it is appropriate to place it in the paraffin fraction. The silver sulfate scrubber removed less than 1% of the C_8 and C_9 paraffins.

Timing and Flow Controls. A flow-switching arrangement, shown in Figure 2, was designed to yield the maximum amount of information with a minimum of equipment. Because the FIA used is a dynamic response instrument that is pressure-sensitive, a dynamic flow system with a minimum of pressure transients is required. Transients introduced by switching between flow paths cause no significant errors. The pressure drop created by the introduction of the flow device also caused no errors larger than instrument reading errors, ∼2 to 3%.

The cycle, shown in Figures 2 and 3, proceeds from low to high concentration at the detector, so that surface effects are minimized. The time required to complete a full cycle is determined by both the dynamic response time of the instrument and the time required for each flow path to reach equilibrium.

In practice these two parameters are indistinguishable on a single instrument. The relative response time of the analyzer is most critical with higher molecular weight materials. This was demonstrated when an instrument with a much smaller "dead" volume between the detector and sample splitter was substituted for the original instrument, Model 109. With the smaller volumes, response times were 10 to 30 seconds, whereas with the larger volume, response times were 30 to 60 seconds.

The longest period of time that a sample may be passed through a scrubber is determined by the time required for the least strongly absorbed material to elute. This elution time shortens as the column becomes saturated with reacted material. This effect limits the effective life of each scrubber, but is not critical in the design of the system.

In the studies reported here 1 to 1¹/₄ minutes in each flow configuration allowed equilibrium response to be attained (with a Model 109A).

An automatic cycling timer was used to control the solenoids allowing automatic operation and ensuring the proper sequence of flows. All solenoid valves, Va, are plumbed so that they are normally off. Air flow for backflush of scrubbers and air purge is controlled by needle valves, N. These flows are not critical as long as no adverse pressure effect is apparent.

Table III. Efficiencies of Solid Absorbents

		Cation[a]			
		Pd	Ag	Hg	Pt
	P.P.M. C	Efficiency, % of Compound Removed			
Ethylene	100	85	98	97	15[b]
Propylene	100	100–70b	99–97b	100–90b	100
Xylene	100	99	99–98b	0–2b	98
Benzene	125	50–10b	99–98b	0	85–25b
Benzene	50			0	
Acetylene	50	20	70	98	20–60b
Nonane	125	0	1	1	0
1-Butene	100	98	99	90+	
1-Butene	10	95	99	90+	

[a] All with H_2SO_4 on firebrick.
[b] Range of several tests on different scrubbers.

Figure 5. Olefin scrubbing efficiency of 40% HgSO₄–20% H₂SO₄
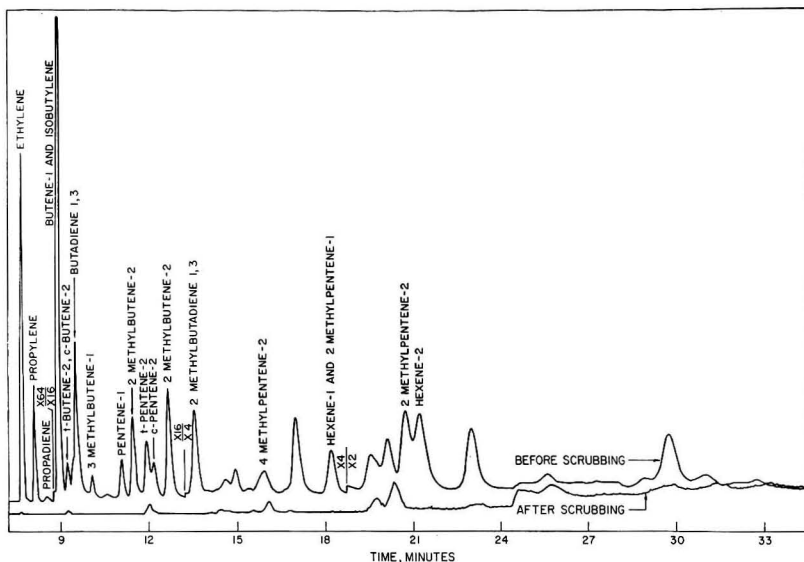
System Evaluation

The response of the flame ionization analyzers used in these studies to aromatics and olefin mixtures was approximately the same as its response to paraffins. Responses to mixtures of 16 different aromatics blended at six different concentration levels were similar to calculated values. Analyses of mixtures of 14 olefins at eight different concentration levels also showed no preferential response.

Some instrumental holdup, usually less than 5% of the total concentration, was found in the capillary splitter of the detector. Approximately 1 hour's flushing with clean air was required to return the instrument to zero after running raw automotive exhaust. This would cause an appreciable error if samples at atmospheric concentrations were analyzed immediately following emission level samples.

Gas chromatographic analyses were made to determine the portions removed by each scrubber. By appropriate valving, the effluent from only one cycle was obtained. Comparison of these collected samples showed that each column removed over 95% of the desired materials. When these samples were run on the gas chromatograph and the results compared with chromatographs of the original sample, no change in concentration was noted for materials which were supposed to pass through the scrubber.

The HgSO₄–H₂SO₄ scrubber passed 90 to 95% of the aromatics with some small losses in the C_{10}^+ region. The effect of this scrubber on olefins is shown in Figure 5, a composite of the chromatograms of the original sample and of the scrubbed sample. The gas chromatographic analysis was run on the olefinic portion of a sample that had been split on a silver nitrate–ethylene glycol precolumn (Bellar *et al.*, 1964). The
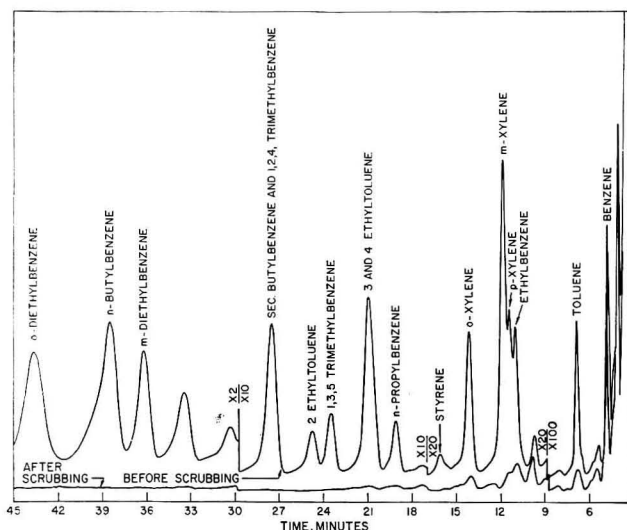
Figure 6. Chromatograms of aromatic fraction before and after scrubbing with PdSO₄–H₂SO₄

analytical column was made of copper coated with dibutyl maleate, 300 feet long and 0.06-inch i.d. It was operated at 0° C., and the total effluent was seen by the flame ionization detector.

The scrubber column of combined $HgSO_4$–H_2SO_4 and $PdSO_4$–H_2SO_4 was equally efficient in removing olefins. More than 95% of the higher aromatics were removed, while over 80% of the benzene passed through. A chromatogram taken on the original sample is compared with that of the scrubbed sample in Figure 6. The peak appearing under toluene for the scrubbed sample is not toluene but an unresolved material, probably paraffinic in the C_8 molecular weight range. This material appears as a shoulder on the direct-sample chromatogram. The analytical column was a Perkin-Elmer MBMA open tubular column 300 feet long and 0.06-inch i.d. operated at 55° C.

Samples of automobile exhaust run by this method have been compared with detailed gas chromatographic analysis of the same samples. The total carbon concentration calculated from the gas chromatographic analysis was 4% higher than that seen by the flame ionization analyzer.

Comparison of the scrubbed fractions with the appropriate gas chromatographic totals showed that the subtractive technique resulted in olefin concentrations approximately 5% high. There was no other discernible pattern to the results. Aromatics and paraffins agreed within ±5%.

Response of Other Organic Materials

The technique was tested with a variety of oxygenated materials (Table IV). Alcohols, acetone, acids, and any compound containing an ethylenic bond elute with the olefins. Aldehydes, ether, esters, and nitrates appear in the aromatic fraction. Methyl ethyl ketone is partially eluted from the olefin scrubber and would be determined in both fractions.

The oxygenated materials studied were strongly adsorbed by the metal system. This caused equilibrium response to occur more slowly than the response for hydrocarbons on the same instrument. This slower response would be noted in exhaust samples as rapid early response from the hydrocarbons followed by a delayed plateau.

A typical display of the results is shown in Figure 3. The reference air is not normally corrected to zero but indicates the amount of surface adsorption that has occurred in the instrument. This value would be significant only if completely dissimilar samples were run consecutively. In normal operation the unit is run through two complete cycles to ensure reproducible results. If the unit is operating properly, results from the duplicate runs will agree within 2%.

In addition to the extensive life test, the system has been operated in routine testing of well over 100 samples.

Calculation

Results are calculated in the following manner:

Total reading = paraffins + olefins + aromatics = T
$HgSO_4$ − H_2SO_4 scrubbed = paraffins + aromatics = Hg
$HgSO_4$ − H_2SO_4, $PdSO_4$ − H_2SO_4 = paraffins + benzene = Pd
T − Hg = olefin concentration (plus acetylene)
Hg − Pd = alkylbenzene concentration
Pd = paraffins + benzene concentration
T = total hydrocarbon concentration

Table IV. Reaction of Miscellaneous Organic Compounds

	Total Concn. as Seen by Analyzer, P.P.M. C	Per Cent Removed	
		$HgSO_4$ − H_2SO_4	$PdSO_4$ − H_2SO_4[a]
Methanol	17	100	100
Ethyl alcohol	160	100	100
Propionaldehyde	120	15	100
Butyraldehyde	84	2	100
Acetone	138	100	100
Methyl ethyl ketone	150	60	100
Ethyl ether	185	0	100
Allyl ether	172	100	100
Acetic acid	46	100	100
Methyl acetate	98	5	100
Ethyl nitrate	58	0	100

[a] $HgSO_4$ − H_2SO_4 prescrubber in series.

The contribution of the oxygenates to the carbon content of untreated automotive emissions is small, and their concentration is further reduced in the sampling system used.

Summary

A simple method has been developed for determining hydrocarbon classes of emissions. A column of 40% $HgSO_4$–20% H_2SO_4 on firebrick removes olefins and acetylenes, and a column of 2% $PdCl_2$–(concentrated H_2SO_4 + 2% H_2O) on firebrick removes the aromatics except benzene. The system can be used in conjunction with regular hydrocarbon analyzers. Absorption and mixing effects are minimized by the high flow rates through the system. The system has a long effective life. Failure is readily indicated by marked changes in color of the scrubbers.

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Modern Instrumental Techniques in the Structure Elucidation of Products Derived from Petrochemicals

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■ The use of infrared, nuclear magnetic resonance, and gas chromatography–mass spectrometry in the solution of a variety of structure-composition problems in petrochemical analysis is illustrated. The structures and stereochemistry of several sulfenyl chloride (RSCL; R = alkyl, aryl, phosphoryl, acetylthio)olefin and diolefin adducts were established using the combined techniques, especially 100-mc. NMR. with frequency sweep decoupling. By use of the gas chromatography–mass spectrometry method, the components of a complex allene chlorination product mixture and several thiol-unsaturate adducts are separated and analyzed "on the fly" by mass spectrometry. These data, supported by NMR and infrared, allow a complete analysis of each system.

Rapid developments during the past decade in analytical instrumentation, notably the introduction of high resolution nuclear magnetic resonance spectroscopy, development of combination gas chromatography–mass spectrometry techniques, and the availability of high resolution infrared spectrophotometers, have revolutionized the field of petrochemical analysis. It is now possible to analyze, rapidly and completely, organic reaction products for structure and composition with these combined techniques using a minimal amount of sample. These developments have obviated the need for long and involved physical separations as well as the application of classical organic characterization techniques such as functional group analysis on separated fractions.

Often complete structure determinations of reaction products, including stereochemistry, can be obtained solely by a detailed study of their NMR spectra. In other cases, supporting evidence such as that provided by infrared or mass spectrometry is necessary to confirm the presence of functional groups or decide problems of stereochemistry. In the analysis of complex reaction mixtures, use of the gas chromatography–mass spectrometry technique complements the other instrumental methods. The individual components (all those >0.1% on a routine basis) resolved by chromatography are analyzed individually in the mass spectrometer. Comparison of these spectra with literature data often leads to unequivocal identifications. Even when these molecular weight and fragmentation data are not sufficient to allow a structural assignment, they often provide enough information materially to aid identifications by the other techniques.

In this paper, the authors describe selected examples from their laboratory of the combined use of these techniques in the solution of structure-composition problems related to petrochemical analysis.

Discussion

Sulfenyl Chloride Chemistry. The addition of alkane and arenesulfenyl chlorides to unsaturated systems has received considerable attention and is comprehensively reviewed by Kharasch (1961) and Kharasch *et al*. (1966). However, recent work in this laboratory (Mueller and Butler, 1966), making use of several instrumental techniques, has led the authors to revise several generally accepted ideas regarding the mechanism of addition to olefins and diolefins.

Sulfenyl Chloride Additions to Simple Olefins. In contrast to the generally accepted Markovnikov adduct orientation, we have recently found predominant anti-Markovnikov addition of methane- and benzenesulfenyl chlorides to terminal alkenes followed by postisomerization of the adducts to the Markovnikov-oriented products (Mueller and Butler, 1966). These findings made necessary a re-examination of the stereochemistry of such additions.

Exclusive trans addition to both norbornene and acenaphthylene was confirmed by NMR analysis of the corresponding sulfenyl chloride adducts. The methine protons adjacent to chlorine and sulfur of the acenaphthylene adduct are a pair of doublets (see Figure 1) with a vicinal coupling constant of 2.3 c.p.s. The magnitude of the coupling is clear evidence of the trans nature of the substituents (Dewar and Fahey, 1963) and serves as a useful probe of the stereochemistry.

Selective trans addition was confirmed by an examination of the 100-mc. NMR spectrum of the benzenesulfenyl chloride–norbornene adduct (Figure 2). At the higher field strength (100 mc.), the spectrum is considerably more resolved than at 60 mc. and the multiplicity of the methine groups, which is crucial in the stereochemical assignment, is readily determined.

The *exo*-methine proton adjacent to chlorine is a double triplet at 3.93 p.p.m. Its position downfield from the magnetically more shielded methine proton next to sulfur at 2.96 p.p.m. is in agreement with correlations of chemical shift with substituent electronegativities (Dailey and Shoolery, 1955; Cavanaugh and Dailey, 1961). The diagnostic NMR parameters are in good agreement with those of other norbornane systems studied (Anet, 1964; Musher, 1963; Subramanian *et al*., 1965). Of particular interest is the long range coupling observed between hydrogen nuclei separated by four bonds which further supports the stereochemical assignment. Coupling between H_2 and *exo*-H_6 of 1.0 c.p.s. (Anet,
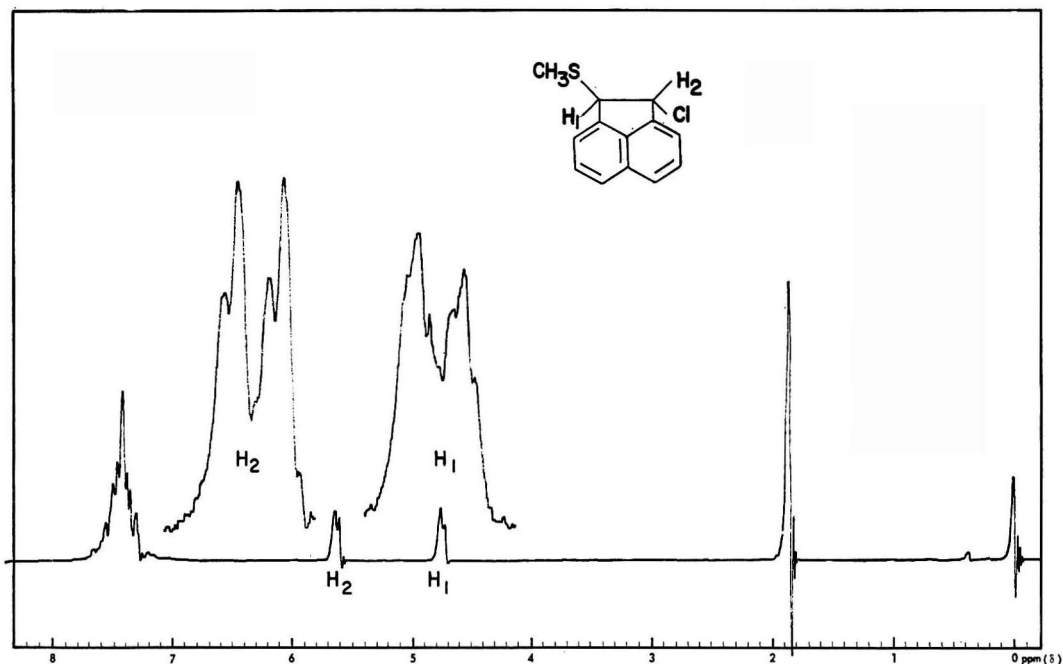
Figure 1. 60-mc. NMR spectrum of benzenesulfenyl chloride–acenaphthylene adduct

1961) is evidence for the exo nature of the methine proton next to chlorine and hence the endo nature of chlorine (the signal appears as a doublet-triplet owing to the similar magnitude of vicinal coupling with H_1 and H_3 further split, long range, by H_6). The methine proton adjacent to sulfur, H_3, is a double doublet. Its endo nature is confirmed by long range coupling with the antibridge proton, H_7, of 2.6 c.p.s. and vicinal coupling of 3.9 c.p.s. In agreement with a considerable body of literature, coupling between the endo proton, H_3, and the adjacent bridgehead proton, H_4, is approximately zero, further pinpointing the endo orientation of H_3.

Rearrangement of sulfenyl chloride adducts to the more stable Markovnikov product on standing was observed in most cases involving additions to simple terminal olefins. This propensity for rearrangement foreclosed attempts at analysis using gas chromatography.

Reaction of acetylthiosulfenyl chloride with propylene, for instance, gave a mixture of I and II. The relative amounts of the isomeric adducts could be simply determined from low temperature NMR analysis of the crude product mixtures. In general, methyl group protons β to chlorine are considerably deshielded relative to those β to sulfur (Butler and Mueller, 1966; Cavanaugh and Dailey, 1961; Dailey and Shoolery, 1955; Mueller and Butler, 1966). The relative intensity of these groups was then used to compute the isomer distribution.

Because of the complexity of the 60-mc. NMR spectra of the isomeric adducts, a complete analysis of the 100-mc. spectrum was undertaken and served as a convenient model for the elucidation of the spectra of the other systems studied.

2,2′	1	3		2,2	1	3
CH$_2$—CH—CH$_3$				CH$_2$—CH—CH$_3$		
Cl	SR	4		4 SR	Cl	
	I—60%				II—40%	

H	δ, P.P.M.	δ, P.P.M.
1	2.98	3.98
2	3.32	2.82
2′	3.70	3.08
3	1.39	1.65
4	2.49	2.49
$J_{1,2}$	10.0	9.0
$J_{1,2}'$	4.0	5.3
J_{2gem}	11.0	14.0
$J_{1,3}$	6.5	6.5

In the 60-mc. spectrum, the methyl group β to sulfur in I is a doublet at 1.39 p.p.m., while the deshielded methyl group β to chlorine in II is a doublet at 1.65 p.p.m. The rest of the 60-mc. spectrum obtained on the mixture is complex because of the overlapping of the A_3MXY and A_3MNX spin systems formed by the methyl, methylene, and methine protons. These higher order systems are due to the presence of an asymmetric center in each molecule in which the adjacent methylene protons are magnetically nonequivalent and have slightly different vicinal coupling constants. Since the geminal coupling constant is large relative to $\partial_2 - \partial_2'$, the ratio $\partial_1 - \partial_2'/J$ is low and the result is a typical AB system. This pair of protons couples unequally with the adjacent methine proton, which is itself coupled with the methyl group protons.

Figure 2. 100-mc. NMR spectrum of 2-endo-chloro-3-exo-phenylthionobornane

$J_{1,2}$ = 4.1 c.p.s.
$J_{2,3}$ = 3.9 c.p.s.
$J_{2,6exo}$ = 1.0 c.p.s.
$J_{3,4}$ = 0
$J_{3,7anti}$ = 2.6 c.p.s.
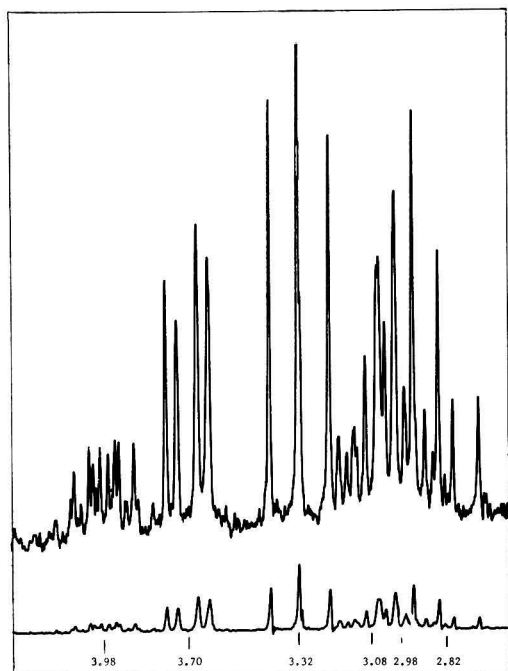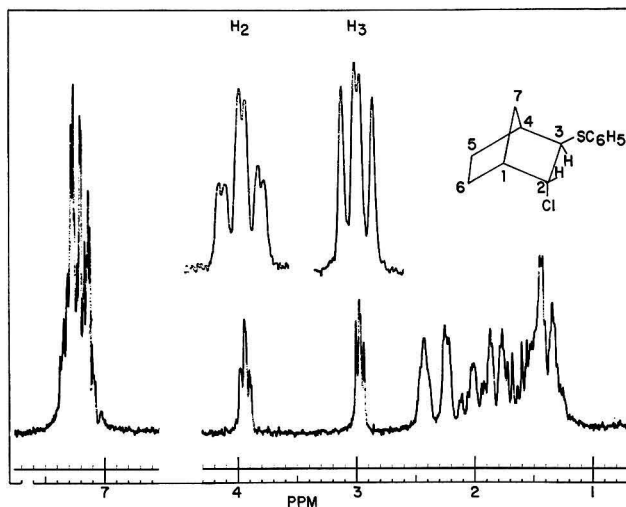
Figure 3. Partial 100-mc. spectrum of acetylthiosulfenyl chloride–propylene adduct

The result is an A_3MNX (A_3MXY) system not amenable to first-order analysis at 60 mc.

At the higher field strength, 100 mc., a simpler spectrum results which can be analyzed by first-order approximations (Pople *et al.*, 1959). Figure 3 shows the methylene-methine region of the propylene adducts; 17 of the theoretical 24 links are now visible.

Considering the spectrum of II, the methylene protons α to sulfur are nonequivalent and appear at a pair of double doublets at 2.82 and 3.08 p.p.m. Their multiplicity is due to the large geminal coupling and unequal coupling with the adjacent methine proton which is a 16-line pattern at 3.98 p.p.m. (each line of the double doublet resulting from coupling with the nonequivalent methylene protons is further split into 1:3:3:1 quartets by the interaction of the methyl group). This methyl-methine coupling was confirmed by spin decoupling of the methyl group at 1.65 p.p.m. The 16-line pattern collapses to the expected double doublet of a simple ABX-type system.

The reverse isomer was shown to have structure I. At 100 mc. an approximately first-order spectrum results, even though the difference in chemical shift between the methine proton (H_1) and one of the nonequivalent methylene protons α to chlorine is only 34 c.p.s.

The methylene protons 2 and 2′ being α to chlorine are deshielded relative to those α to sulfur and appear as a pair of double doublets at 3.32 and 3.70 p.p.m. The upfield double doublet appears as a "triplet" owing to the coincidence of the internal lines caused by the nearly equal geminal and vicinal coupling constants. The methine proton of I is again a 16-line pattern owing to further coupling with the β-methyl group (only 11 of the 16 lines are visible because of overlapping with peaks of the methylene protons of the reverse isomer).

Sulfenyl Chloride Additions to Diolefins. The addition of sulfenyl chlorides to conjugated dienes yields 1,2 adducts with Markovnikov orientation (Mueller and Butler, 1966). In contrast to most known radical and ionic additions, sulfenyl chloride additions do not give 1,4 adducts. Brintzinger and Ellwanger (1954) reported the addition to cyclopentadiene assuming a 1,4 mechanism which we have shown to be incorrect on the basis of detailed instrumental analysis.

Reaction of 1,3-butadiene with acetylthiosulfenyl chloride yields a single adduct, III, which is derived from Markovnikov 1,2 addition.

The stereochemistry of addition was determined by an exam-
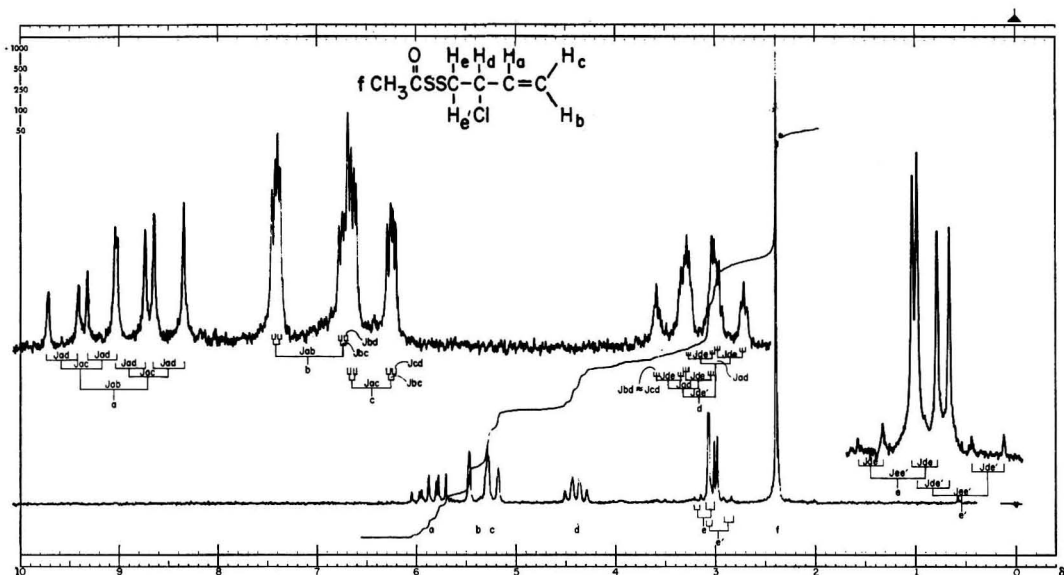
Figure 4. 100-mc. NMR spectrum of acetylthiosulfenyl chloride–butadiene adduct

J_{ab} = 17.0 c.p.s. $J_{c,d}$ = 0.6 c.p.s.
J_{ac} = 10.0 c.p.s. $J_{d,e}$ = 6.2 c.p.s.
J_{ad} = 7.5 c.p.s. $J_{d,e'}$ = 8.0 c.p.s.
$J_{b,c}$ = 1.4 c.p.s. $J_{e,e'}$ = 16.5 c.p.s.
$J_{b,d}$ = 0.8 c.p.s.

ination of the infrared spectrum of the product. Normal ionic addition would be expected to yield a 1,4 adduct having a trans-disubstituted double bond. Bands for this type olefin were absent. However, strong support for a terminal vinyl group derived from 1,2 addition was received from characteristic bands (Bellamy, 1960) in the infrared.

This conclusion was confirmed by an analysis of the 100-mc. NMR spectrum (Figure 4) and the results of several frequency sweep decoupling experiments. These data give a unique solution for the structure and stereochemistry of III.

$$\begin{array}{c} \quad\quad O \quad\quad\quad H_a \; H_c \\ \quad\quad \| \quad e,e'd \quad | \quad | \\ f\; CH_3CSS{-}CH_2CHC{=}C{-}H_b \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad\; Cl \\ \quad\quad\quad\quad III \end{array}$$
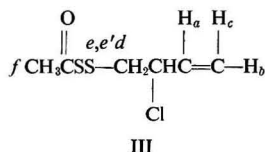
	NMR		Infrared
H	δ, p.p.m.	Cm.$^{-1}$	Group
a	5.90	1645	C=C str.
b	5.40	3100	=CH$_2$ str.
c	5.25	3015	=CH— str.
d	4.42	985	=CH— oop def.
e	3.12	925	=CH$_2$ oop def.
e'	2.97		
f	2.42		

The methylene protons adjacent to sulfur are nonequivalent because of the asymmetry of the molecule and appear as a pair

of double doublets (the typical *AB* pattern of an *ABX* type spin system) at 3.12 and 2.97 p.p.m. Their multiplicity is due to the large geminal coupling and unequal vicinal coupling with the adjacent allylic methine proton, H_d, at 4.42 p.p.m. This proton in turn is coupled with the internal vinylic proton, H_a, and long range to the two nonequivalent terminal methylene protons (H_b, H_c). These vinylic protons appear as a typical terminal vinyl pattern. Proton H_a is a doublet of a double doublet at 5.90 p.p.m. while the more shielded methylene protons, also doublets of double doublets, are at 5.40 (H_b) and 5.25 p.p.m. (H_c).

These assignments were confirmed by frequency sweep decoupling experiments. Triple irradiation of H_e and H_e' (Figure 5) collapses the 32-line multiplet (doublet of a double, double, double doublet) to a doublet further split by the residual allylic coupling into double doublets. The pattern for the terminal vinyl protons remains the same except for some line broadening due to the presence of a strong irradiating secondary source.

Irradiation of *d* decouples *d* from *e* and *e'* to give the expected *AB* pattern shown in Figure 5. Under the irradiation conditions (irradiation with two oscillators of low amplitude on band *d*, each located near the center bands of the quartet to reduce beta frequencies) *d* is not completely decoupled from the vinyl protons as evidenced by the broad absorption appearing between the transition lines assigned to these protons. However, Figure 5 shows that irradiation does remove coupling between the allylic and vinyl protons. The internal vinyl proton is now a double doublet due to trans coupling of 17.0 c.p.s. and cis coupling of 10.0 c.p.s., with the terminal methyl-

ene protons. The patterns for these protons are simplified and now appear as a pair of double doublets. All of the parameters are in good agreement with literature data (Brügel *et al.*, 1960; Gutowsky *et al.*, 1959; Lauterbur and Kurland, 1962).

Sulfenyl Chloride Addition to Allene. Another interesting example from our work on the addition of sulfenyl chlorides to unsaturates is the selective anti-Markovnikov addition of dimethylphosphorylsulfenyl chloride to allene (Mueller *et al.*, 1966).

The determination of the mass spectrum established the monoadduct nature of IV and gave useful information about its gross structural features. It had a molecular ion at m/e 216 with isotope peaks of the correct intensity to establish the molecular formula $C_5H_{10}O_3ClPS$. Characteristic fragments ions were found for the loss of chlorine and for the $(CH_3O)_2$ $P(O)SH^+$ and $^+CH_2Cl$ groups. These data led to the tentative assignment of IV for the adduct structure.

The infrared spectrum (Bellamy, 1960) of IV gives good sup-
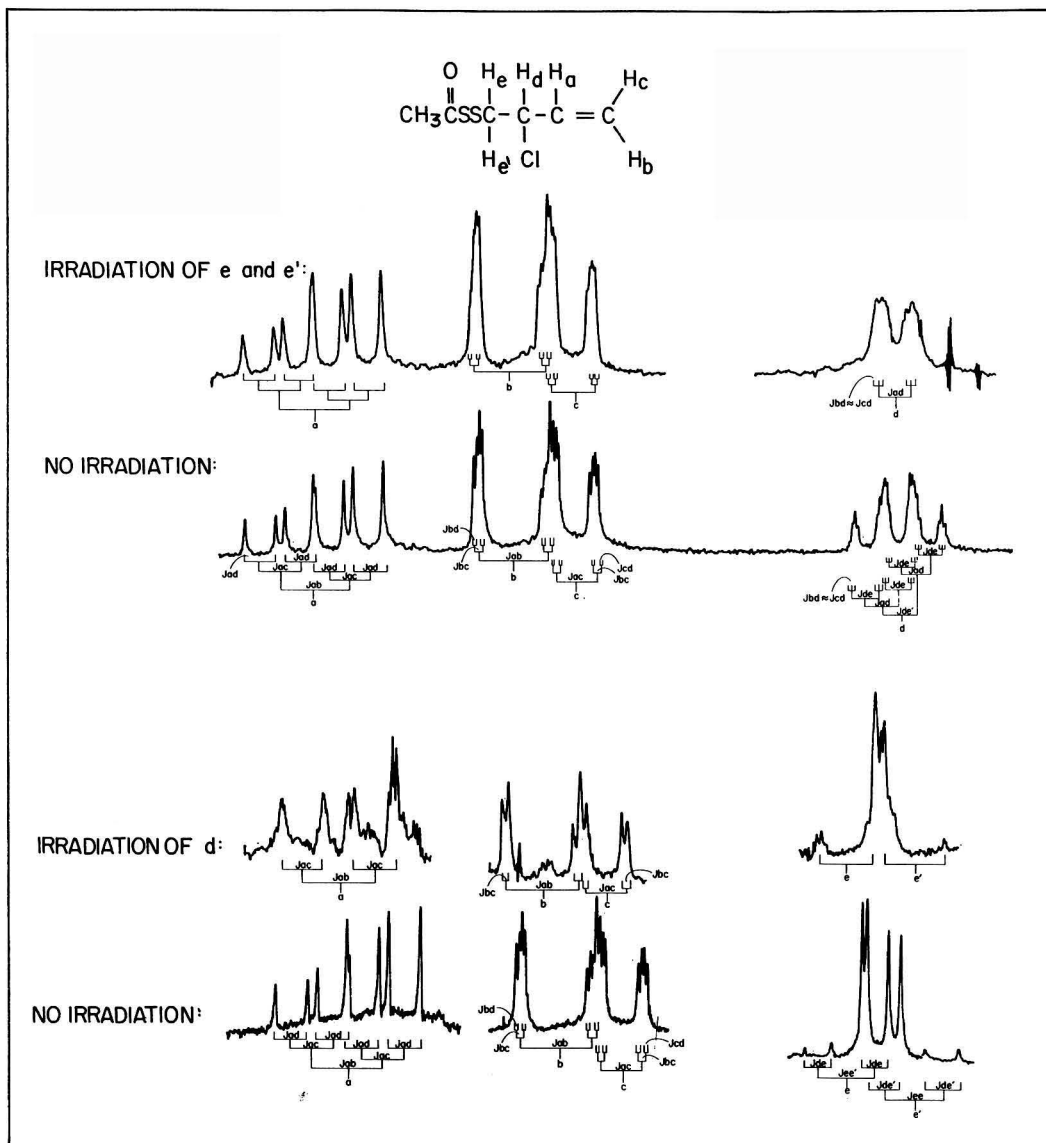
Figure 5. Partial 100-mc. NMR spectrum of acetylthiosulfenyl chloride–butadiene adduct
Spin decoupling

porting evidence for a terminal disubstituted olefin and confirms the presence of the thiophosphate group. However, these data do not allow an assignment of the adduct orientation (Markovnikov or anti-Markovnikov). This question was firmly resolved by a detailed study of the NMR spectrum (Figure 6).

$$
\begin{array}{c}
H_b \quad\quad\quad\quad CH_2Cl \\
C\!=\!C \\
H_a \quad\quad\quad\quad SP(O)(OCH_3)_2 \\
\mathbf{IV}
\end{array}
$$
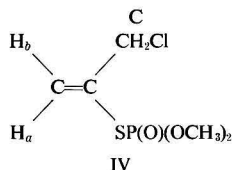
H	NMR δ	Infrared Cm.$^{-1}$	Group
a	5.98 p.p.m.	3090	=CH$_2$ str.
b	5.73	930	=CH$_2$ oop def.
c	4.32	1612	C=C str.
$J_{a,c}$	1.35 c.p.s.	1260	P=O str.
$J_{b,c}$	0.65	1880	C—C str.
$J_{a,b}$	<0.3	1025	P—O str.
J_{p-a}	3.5		
J_{p-b}	4.1		
J_{p-c}	1.93		

The nonequivalent terminal methylene protons of IV appear as a pair of double triplets. Each proton is coupled long range to phosphorus with the larger coupling being tentatively assigned to those groups in trans juxtaposition. Each line of this doublet is then split into triplets by allylic coupling. Again the larger J value is tentatively assigned to trans coupling, although several cases are reported where these values are reversed in simpler systems (Emsley *et al.*, 1966). The allylic methylene protons adjacent to chlorine (H$_c$) are a doublet of a double doublet (the two interior lines overlap) owing to the allylic coupling and interaction with the phosphorus nuclei.

Analysis of Complex Reaction Mixtures

Determination of Allene Chlorination Products. The utility of the gas chromatography–mass spectrometry method in analyzing complex reaction mixtures is illustrated by the identification of all components over 0.1% concentration in a multicomponent allene chlorination product (Table I). Each component of the mixture was separated by gas chromatography (Figure 7) and then individually monitored directly into the mass spectrometer where spectra are determined "on the fly." These spectra are usually comparable to published spectra such as the collections provided by the American Petroleum Institute and the Manufacturing Chemists Association (some 4000+ of these and other mass spectra are available on microfilm in our laboratory). In addition to these data, McLafferty (1962, 1963) has published general rules for predicting spectra of chlorinated hydrocarbons.

In several cases spectral similarities of isomeric materials or the absence of authentic spectra necessitated obtaining sup-
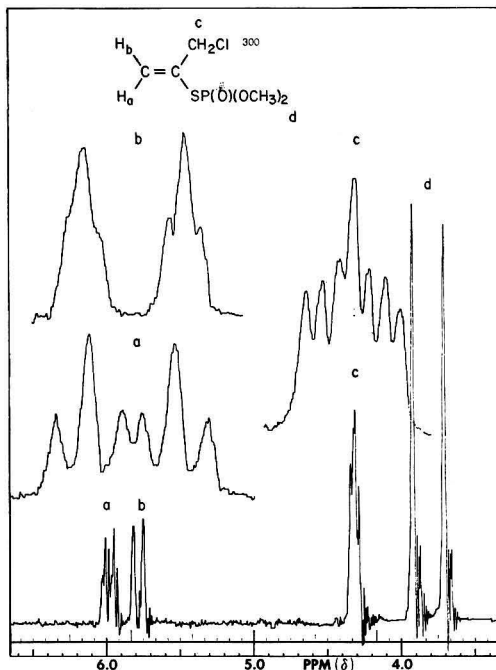
Figure 6. 60-mc. NMR spectrum of *O,O'*-dimethyl-2-*S*-3-chloropropenyl thiophosphate
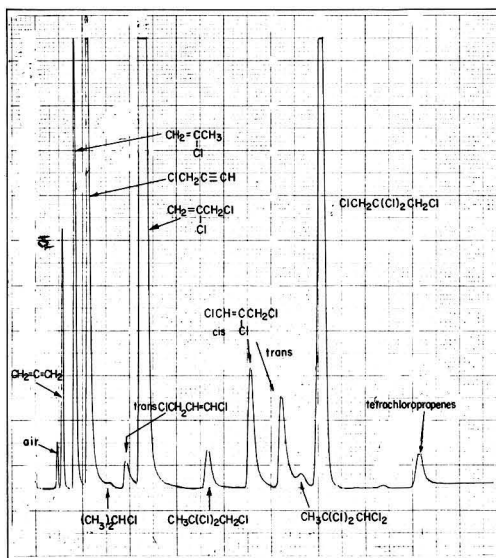
Figure 7. Gas chromatogram of allene chlorination products
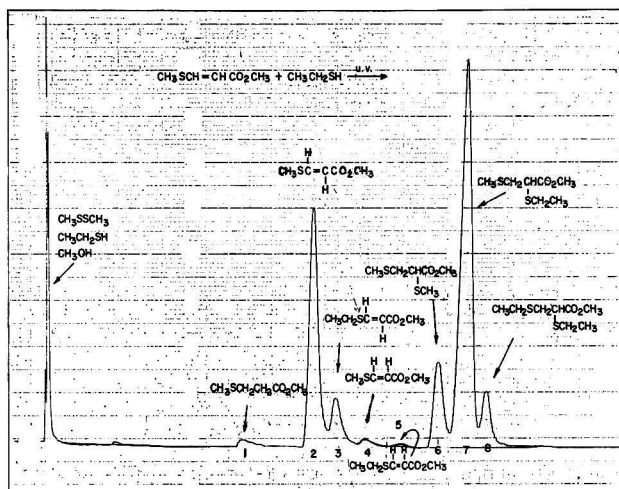
Figure 8. Gas chromatogram of ethanethiol-β-methylmercaptoacrylic acid methyl ester reaction products

Table I. Molecular Ion and Characteristic Fragment Ions of Allene Chlorination Products

Major Products	Molecular Ion (Formula)	Significant Fragment Ions

CH$_3$C≡CH$_2$
   |
   Cl
	m/e 76 (C$_3$H$_5$Cl)	m/e 61 (M-CH$_3$); m/e 41 (M-Cl); m/e 39 (41-H$_2$)

ClCH$_2$C≡CH	m/e 74 (C$_3$H$_3$Cl)	m/e 73 (M-H); m/e 47 (CHCl); m/e 39 (C$_3$H$_3$)
ClCH$_2$CH=CHCl	m/e 110 (C$_3$H$_4$Cl$_2$)	m/e 75 (M-Cl); m/e 49 (CH$_2$Cl); m/e 39 (C$_3$H$_3$)

CH$_2$=CCH$_2$Cl
    |
    Cl
	m/e 110 (C$_3$H$_4$Cl$_2$)	m/e 75 (M-Cl); m/e 61 (M-CH$_2$Cl); m/e 49 (CH$_2$Cl); m/e 39 (C$_3$H$_3$)

CH$_3$C(Cl)$_2$CH$_2$Cl	m/e 146 (C$_3$H$_5$Cl$_3$)	m/e 111 (M-Cl); m/e 97 (M-CH$_2$Cl); m/e 75 (111-HCl); m/e 49 (CH$_2$Cl)

ClCH=C—CH$_2$Cl (c&t)
      |
      Cl
	m/e 144 (C$_3$H$_3$Cl$_3$)	m/e 109 (M-Cl); m/e 83 (CHCl); m/e 73 (109-HCl)

CH$_3$C(Cl)$_2$CHCl$_2$	m/e 180 (C$_3$H$_4$Cl$_4$)	m/e 165 (M-CH$_3$); m/e 145 (M-Cl); m/e 97 (CH$_3$C(Cl)$_2$); m/e 83 (CHCl$_2$)
ClCH$_2$C(Cl)$_2$CH$_2$Cl	m/e 180 (C$_3$H$_4$Cl$_4$)	m/e 145 (M-Cl); m/e 144 (M-HCl); m/e 131 (M-CH$_2$Cl); m/e 109 (145-HCl)

Table II. Characteristic Mass Spectral Parameters of Mono- and Diadducts

	Compound	Molecular Ion M^+	Formula	Characteristic Fragment Ions, m/e
I c,t	$CH_3SCH{=}CHCO_2CH_3$	132	$(C_5H_8O_2S)$	117 (M-CH$_3$); 100 (M-OCH$_3$); 85 (M-CH$_3$S); 73 (M-CO$_2$CH$_3$)
II c,t	$CH_3CH_2SCH{=}CHCO_2CH_3$	146	$(C_6H_{10}O_2S)$	117 (M-CH$_2$CH$_3$); 115 (M-OCH$_3$); 100 (115-CH$_3$); 87 (M-CO$_2$CH$_3$)
III	$CH_3SCH_2CH(SCH_3)CO_2CH_3$	180	$(C_6H_{14}O_2S_2)$	133 (M-CH$_3$S); 132 (M-CH$_3$SH); 121 (M-CO$_2$CH$_3$); 101 (132-CH$_3$O); 61 (CH$_3$SCH$_2^+$)
IV	$CH_3SCH_2CH(SCH_2CH_3)CO_2CH_3$	194	$(C_7H_{16}O_2S_2)$	135 (M-CO$_2$CH$_3$); 133 (M-C$_2$H$_5$S); 132 (M-CH$_3$CH$_2$SH); 101 (132-OCH$_3$); 61 (CH$_3$SCH$_2^+$)
V	$CH_3CH_2SCH_2CH(SCH_2CH_3)CO_2CH_3$	208	$(C_8H_{18}O_2S_2)$	149 (M-CO$_2$CH$_3$); 147 (M-C$_2$H$_5$S); 133 (M-CH$_3$CH$_2$SCH$_2$); 75 (CH$_3$CH$_2$SCH$_2$)$^+$

Table III. NMR Parameters of Thiol-β-mercaptoacrylic Acid Methyl Ester Adducts

$RSCH{=}CHCO_2CH_3$ (β α) I, II
$RSCH_2CH(SR')CO_2CH_3$ (β α) III, IV, V

			R			R'						$J_{\alpha\beta}$,
Structure	R	R'	CH$_3$	CH$_3$	CH$_2$	CH$_3$	CH$_3$	CH$_2$	CO$_2$CH$_3$	Hα	Hβ	C.p.s.
I cis	CH$_3$		s2.12						s3.73	d5.78	d7.06	10.3
I trans	CH$_3$		s2.35						s3.68	d5.76	d7.71	15.0
II cis	C$_2$H$_5$			t1.34	q2.85^a				s3.66	d5.68	d7.12	10.5
II trans	C$_2$H$_5$			t1.34	q2.85^a				s3.66	d5.88	d7.67	15.3
III	CH$_3$	CH$_3$	s2.14			s2.14			s3.73	dd3.42	2.95^b 2.66	9.2, 5.8^c
IV	CH$_3$	C$_2$H$_5$	s2.11				t1.23	q2.65^a	s3.72	dd3.43	2.97^b 2.65	9.3, 5.9^c
V	C$_2$H$_5$	C$_2$H$_5$		t1.23	q2.55^a		t1.23	q2.66^a	s3.73	dd3.39	2.98^b 2.69	10.5, 6.2^c

^{a} J CH$_2$—CH$_3$ = 7.5 c.p.s. ^{b} Protons nonequivalent and form with the adjacent methine proton an ABX spin system. Their signals appear as a pair of overlapping quartets. ^{c} J_{gem} = 13.0 c.p.s.
Notation: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet

porting evidence. Nuclear magnetic resonance and infrared data obtained on the entire reaction mixture usually allowed definitive structural assignments for the major components. For materials present at lower levels, the mass spectral evidence often narrows the choice to a few candidates. These materials are then obtained and spectral and gas chromatographic comparisons made.

The infrared spectrum of the product mixture revealed the presence of the terminal triple bond of propargyl chloride (3010 cm.$^{-1}$ ≡CH str.; 2125 cm.$^{-1}$ C≡C str.) and the type III olefin system of 2,3-dichloro-1-propene (3090 cm.$^{-1}$, =CH$_2$ str.; 1632 cm.$^{-1}$, C=C str. and 895 cm.$^{-1}$, =CH$_2$ oop def.) (Bellamy, 1960). In addition, there were a variety of minor bands due to unsaturation. The NMR spectrum confirmed the presence of these components as well as several others [the NMR parameters are listed below and are in agreement with published data on related compounds (Emsley *et al.*, 1966)].

Analysis of Thiol-Unsaturate Adducts. The addition of

NMR Parameters

Structure		Chemical Shift, P.P.M.	
H$_a$	H$_b$	H$_a$	H$_b$
$CH_2{=}C(Cl){-}CH_2Cl$		5.57, 5.38	4.13
$HC{\equiv}C{-}CH_2Cl$		2.47	4.06
$ClCH_2{-}C(Cl)_2{-}CH_2Cl$		4.13	4.13
c CH(Cl)=C(Cl)—CH$_2$Cl		6.37	4.65
t CH(Cl)=C(Cl)—CH$_2$Cl		6.64	5.09

ethanethiol to β-methylmercaptoacrylic acid methyl ester results in the formation of several products (I to V) by a combination of direct addition and allylic reversal–type mechanisms (Mueller, 1966).

Data obtained from several instrumental methods were used

in complementary manner to determine the structure and stereochemistry of I to V and illustrate further the versatility of the techniques in the analysis of complex reaction mixtures.

Separation of each component was achieved using a Dowfax column and the components were analyzed by mass spectrometry (Table II gives a summary of the mass spectral parameters). This method gave useful structural and composition data.

The first peak in the gas chromatogram (Figure 8) was identified by its characteristic mass spectrum as β-methylmercaptopropionic acid methyl ester, an impurity formed by the addition of methanethiol to methyl acrylate during synthesis of I (methyl acrylate is an impurity in methyl propiolate).

Peaks 2 and 4 were identified as trans- and cis-I, both by their retention time and by their characteristic mass spectra (see Table II).

Peaks 3 and 5 also had identical mass spectra, typical of isomeric materials. Their molecular ion at m/e 146 ($C_6H_{10}O_2S$) and fragment ions due to the loss of $CH_3CH_2 \cdot$, $CH_3O \cdot$, and $CH_3CO_2 \cdot$ led to the tentative assignment of trans- and cis-II for their structure. This assignment was supported by an independent synthesis of this mixture by the addition of ethanethiol to methyl propiolate. The infrared spectrum (987 cm.$^{-1}$, H—C≡C—H oop def.; 3015 cm.$^{-1}$, ≡CH— str.; 1578 cm^{-1}, C≡C str.) (Bellamy, 1960) and NMR spectrum (Figure 9) of this sample confirmed the predominant trans configuration of II (Table III gives a summary of the NMR parameters of the thiol adducts). These peaks were coincident with those in the spectra of the product mixture; in addition, admixture of II to

the product enhanced only peaks 3 and 5 in the gas chromatogram.

The mass spectrum of peak 6 gave a molecular ion at m/e 180 ($C_6H_{14}O_2S_2$) and had characteristic fragment ions for the loss of $CH_3S \cdot$, CH_3SH, and $CH_3CO_2 \cdot$; and had a prominent ion at m/e 61 for the $CH_3SCH_2^+$ fragment. This information led to the tentative assignment of the α,β-dimethylmercapto structure (III) for the peak. This was confirmed by independent synthesis of III. Its NMR spectrum is reproduced in Figure 10. The methylene protons of this compound are nonequivalent because of the adjacent asymmetric center and form with the methine proton an overlapping ABX-type spin system. Their signals appear as a pair of overlapping quartets at 2.95 and 2.66 p.p.m. while the methine proton is a double doublet, with two small wings of low intensity owing to combination lines at 3.43 p.p.m. ($J_{AX} = 9.2$, $J_{BX} = 5.8$, and J_{gem} 13.0 c.p.s.). The solution of the NMR spectrum of this material was used as a model for the analysis of the more complicated spectra of IV and V (in these cases the β-methylene protons overlap with the S-ethyl groups).

Peak 7, the major reaction product, was identified using a variety of techniques. The mass spectrum had an intense molecular ion at m/e 194 ($C_7H_{16}O_2S_2$) establishing a gross methylethyl dimercapto adduct structure. An analysis of the NMR spectrum of the reaction mixture indicated structure IC for this adduct. It had a methylene-methine resonance pattern similar to that of III. In addition, characteristic peaks for the S-ethyl group are at 1.23 p.p.m. (CH_3CH_2S) and 2.65 p.p.m. ($—CH_2S$). Comparison of the GC retention time and NMR spectrum
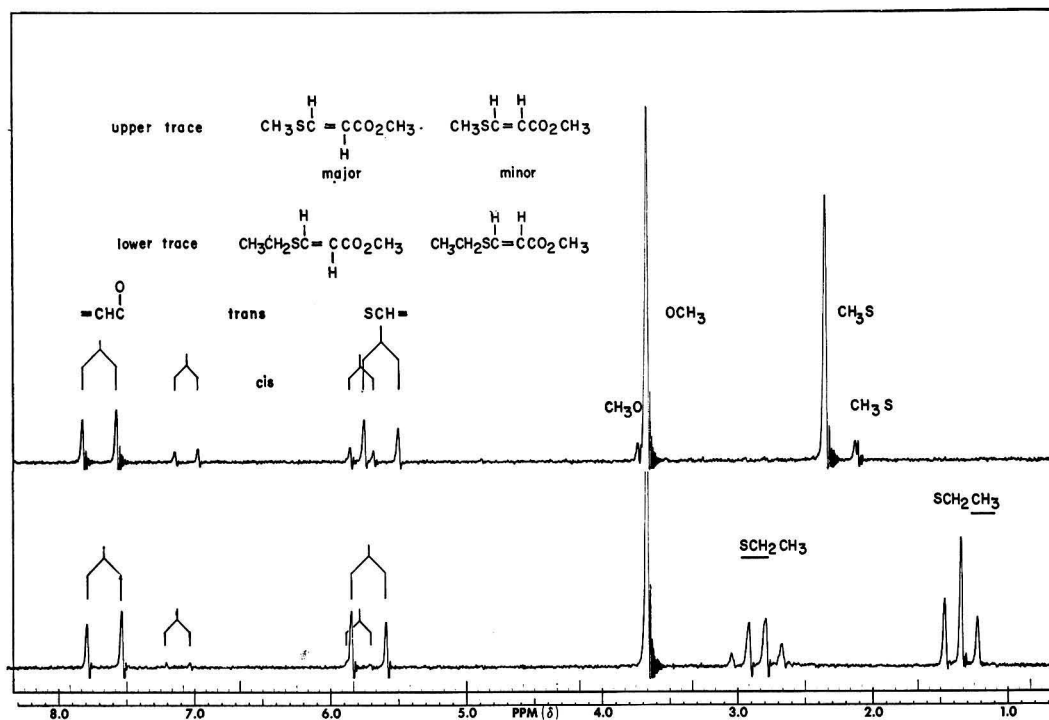
Figure 9. 60-mc. NMR spectra of cis- and trans-β-methyl- and β-ethylmercaptoacrylic acid methyl esters
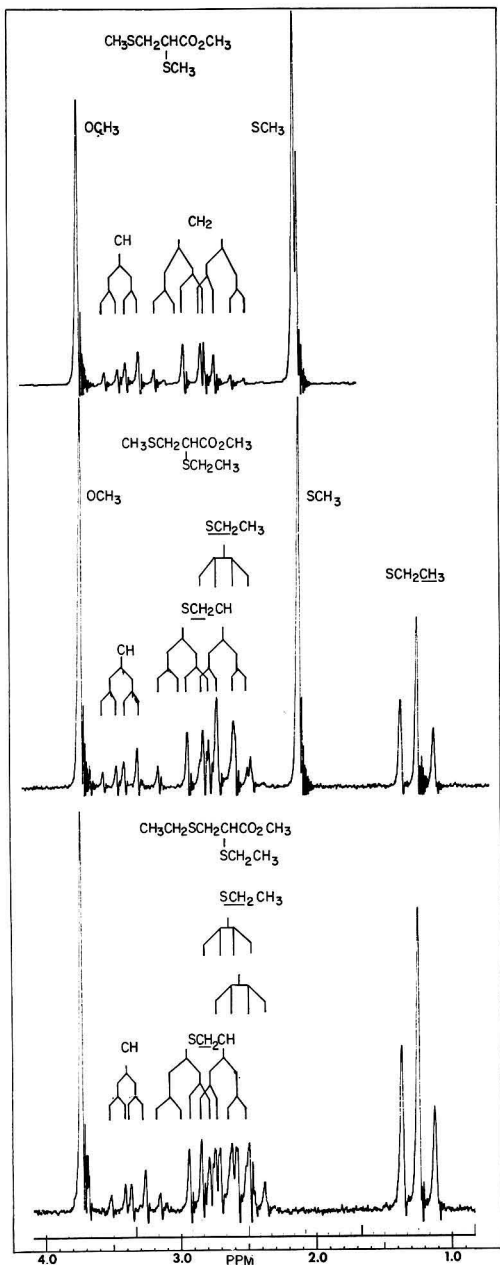
Figure 10. 60-mc. NMR spectra of α,β-diadducts

(Figure 10) of the authentic material gave confirming evidence for the assignment.

The last peak (peak 8) had a molecular ion at m/e 208 ($C_8H_{18}O_2S_2$), establishing a gross diethylmercapto diadduct structure. Intense peaks at m/e 133 (M—$CH_3CH_2SCH_2\cdot$) and m/e 75 ($CH_3CH_2SCH_2^+$) led to the tentative assignment of the α,β structure (rather than an α,α or β,β structure). This evidence was confirmed by independent synthesis and comparison of spectral and chromatographic parameters.

Conclusions

These combined techniques are useful in the solution of a wide variety of problems relating to petrochemical analysis. The gas chromatography–mass spectrometry method is particularly useful in analyzing complex mixtures. Mass spectral data derived from these analyses allow the postulation of certain gross formulas and often the exact structure of components present in as little as 0.1 % on a routine basis. Ancillary use of capillary gas chromatography and/or rapid scan infrared, which are under development in this laboratory, promise further to broaden the scope of the method. Rapid developments in nuclear magnetic resonance theory and instrumentation will increase the utility of this method in the characterization of petrochemicals. Infrared continues to be invaluable as a probe of subtle structural features.

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Gas Sorption by Suspensions of Activated Carbon in Water

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■ Gas scrubbing by suspensions of adsorbent particles in liquids offers the advantages of high capacity, fluid handling, and inexpensive solvent losses. Reported herein are the results of adsorption capacity for carbon dioxide, butane, and propane on wet-activated carbon. Also reported are the results of mass transfer efficiency for carbon dioxide, methane, propane, butane, *n*-hexane, ethylene, trichloroethylene, benzene, toluene, butyl alcohol, amyl alcohol, and acetone sorption by suspensions of activated carbon in water. The efficiency results agree with those predicted by a mathematical model. Solubility of the transferring component in water is the major factor affecting transfer rate. Adsorption capacity may be as high for wet-activated carbon as for dry, depending on the gas.

I n recent years a demand has been placed on gas purification with the increasing realization of the effects of gaseous pollutants. These pollutants may simply be a source of nuisance or they may have detrimental effects upon human health, plants, animals, and materials (corrosion). Some of the important gaseous impurities are nitrogen oxides, sulfur oxides, carbon oxides, hydrocarbons, aldehydes, and ketones, organic and inorganic acids, organic halides, ammonia, and special compounds specifically related to certain industries. The requirement of low level of these impurities in large volumes of low pressure gas, with regard to air pollution abatement, spurs us to consider new approaches to gas purification.

This paper describes a preliminary investigation of gas scrubbing by suspensions of activated carbon in water. To our knowledge, this is the first time the use of suspensions of adsorbent particles in liquid has been investigated for gas scrubbing, and hence it is exploratory in nature.

The primary operation of the gas purification processes frequently falls into one of the following four categories:

1. Absorption into a liquid
2. Adsorption on a solid
3. Chemical conversion (reversible or irreversible) to another compound
4. Other processes, such as condensation, etc., for specific applications

There are problems and disadvantages associated with these methods. Easy handling of liquids for absorption is marred by its generally low capacity for physical sorption, while exactly the opposite is true in the case of solids for adsorption. One constituent of a gas mixture may be separated by absorption in a liquor with which it undergoes a reversible or irreversible chemical reaction. In this case the advantage over a process involving physical absorption is much higher capacity; however, the disadvantages are corrosion problems, expensive solvent losses in regenerating the liquor, or the chemical cost for irreversible reaction.

The point of inception of the present research was the concept of combining the favorable characteristics of both types of systems. If the wet adsorbent can retain its high adsorptive capacity, one can combine the advantages of easy handling, inexpensive solvent losses, and high capacity. Besides, adsorption has the advantage of applicability to the removal of a wide variety of organic compounds.

An extensive body of literature exists for absorption and adsorption studies individually, yet little is known of adsorption and absorption as a combined process—i.e., "sorption" by suspensions. After the work of Findlay in 1910, the study of sorption by suspensions has been reported only since 1951 (Munemori, 1951; Nagy and Dezso, 1959; Nagy and Schay, 1958; Pozin *et al.*, 1957; Tibor *et al.*, 1956) with most of the work reported from Hungary, with a view to improving the understanding of catalytic reactions.

Objectives

The objective of this research was to study and analyze the process of mass transfer as applied to gas sorption by suspension of adsorbent particles in liquid. Major factors of interest are equilibrium relationships and rates of transfer. In gas transfer to suspension of adsorbent particles the solute gas first dissolves in the absorbent and from the liquid it is adsorbed by the adsorbent particles. Thus, there are transport steps from gas to interface, through liquid, from liquid to solid, and through solid. A useful adsorption capacity on the wet solid is necessary, but high equilibrium capacity does not ensure high transport rates. The rates and the factors affecting rates must be investigated.

Equilibria were determined in batch and in flow systems. Rates of sorption were measured in small bubblers in which gas is passed through a column of suspension. The choice of the bubbler was governed by the requirement of a simple system in which a comparative study of rates of sorption for a large number of gases could be made. The bubbler also provides some similarity to practical contacting devices, such as sieve plates, while allowing one to investigate the mechanism of transfer and the controlling factors. The effect of adsorbent concentration on the rates of sorption was investigated. This study included a number of organic gases and vapors to cover the range of solubility and adsorption.

Mathematical Representations

We first investigate the transfer to the liquid and then take into account the presence of the adsorbent particles in liquid. Gas is dispersed through a sintered glass plate and bubbles in contact with the liquid tend toward equilibrium with the liquid at a finite rate. After a sufficiently long time of contact, equilibrium is reached and a limiting quantity of pollutant has

transferred from the gas to the liquid. In a short time of contact only a fraction, f, of this maximum mass is transferred.

$$f = \frac{P_i - P_e}{P_i - P_1} \tag{1}$$

To predict the intrinsic efficiency, f, of a bubbler we must take into account the physical behavior of bubbles in a liquid. Though there exist a bubble size distribution and a residence time distribution of bubbles in a bubbler, one can take an average bubble size and an average residence time, because the distributions are narrow (Calvert and Workman, 1961). If it is assumed that each bubble comes in contact with liquid of constant average composition during its entire period of rise, t_r, the change of soluble component concentration in a bubble is given by:

$$\int_{P_i}^{P_e} \frac{dP}{(P - P_1)} = - \int_0^{t_r} \frac{P_T}{HM_B} \cdot K_L \cdot 4\pi r^2 \cdot dt \tag{2}$$

where $P = HC$, definition of Henry's law constant
C = concentration of dissolved gas in liquid bulk, moles of gas per cc. of liquid

$$M_B = \left(\frac{4}{3}\pi r^3\right) \bigg/ (P_T/RT)$$

or

$$P_e = e^{-\left[\frac{3}{Hr}\frac{RT}{} \cdot K_L \cdot t_r\right]} \cdot (P_i - P_1) + P_1 \tag{3}$$

Therefore,

$$f = 1 - e^{-\left[\frac{3}{Hr}\frac{RT}{} \cdot K_L \cdot t_r\right]} \tag{4}$$

In the case of a sparingly soluble gas the over-all mass transfer coefficient, K_L, can be identified with the liquid phase mass transfer coefficient, k_L. The transfer coefficient from the interface into liquid is described fairly well by Higbie's penetration theory (1935) as

$$k_L = \sqrt{\frac{2 DU_B}{\pi r}}$$

The time of contact or surface renewal is taken as $(2 r/U_B)$, the time required for a bubble to rise through one diameter of height.

When adsorbent particles are present in the liquid, the transfer of gas to the supension can be viewed to take place in the following manner:

1. The solute gas diffuses from the bulk of the gas phase to the gas-liquid interface.
2. From the gas-liquid interface it diffuses to the bulk of liquid.
3. The diffused gas mixes in the bulk.
4. From the bulk of the liquid, through the liquid film surrounding the adsorbent particle, the dissolved gas diffuses to the particle surface.
5. Diffusion through the liquid, in the pore, to the pore internal surface.

For simplification, it is assumed that the presence of adsorbent particles does not affect the first two steps. Hence
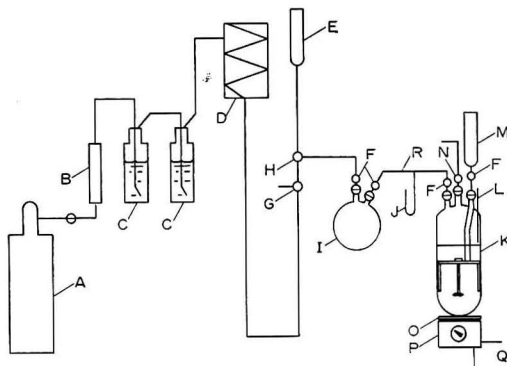
Figure 1. Experimental system for batch method

A. Gas cylinder. B. Rotameter. C. 500-cc. bubbler. D. 12-foot 3/8-inch copper tube heat exchanger. E. 250-cc. buret with 1-cc. graduations. F. 2-Way Teflon stopcock. G. 3-Way glass stopcock. H. 3-Way glass stopcock. I. 2-Liter reservoir flask. J. Manometer. K. 1-Liter cylindrical reaction flask. L. Thermometer. M. 500-Cc. buret with ball joint. N. Teflon stopcock. O. Insulator. P. Magnetic stirrer. Q. Cooling air. R. Teflon connecting tube.

Equation 4 is still valid and accounts for the first two steps. Instantaneous bulk mixing is assumed to eliminate step 3. The last two steps can be represented by the following equation:

$$N_A = AK_c\left[\frac{P_1}{H} - \frac{P_c}{H}\right] \tag{5}$$

Equation 5 can be combined with the equation for the Freundlich-type adsorption isotherm, such as

$$V = aP^n$$

to give

$$\frac{dP_c}{dt} = \frac{RTP_c^{(1-n)}}{HP_TV_c \cdot a \cdot \rho \cdot n}(AK_c)(P_1 - P_c) \tag{6}$$

The two rate equations (Equations 4 and 6), along with the over-all mass balance, would complete the description of mass transfer to the suspensions. The over-all mass balance is as follows:

$$\int_0^t (P_i - P_e)Gdt = V_1\frac{RT}{HP_T} \cdot P_1 + P_c^n \cdot a \cdot w \tag{7}$$

Equations 3, 6, and 7 are difficult to solve simultaneously because of nonlinearity; however, they can be written in a convenient form as given below and a computer solution of them can be obtained for given initial conditions.

$$\frac{dP_e}{dt} = f \cdot \frac{dP_1}{dt} \tag{8}$$

$$\frac{dP_1}{dt} = \frac{HP_T}{RT} \cdot \frac{1}{V_1} \times$$
$$\left[G \cdot (P_i - P_e) + a(AK_c) \cdot \frac{RT}{HP_T}(P_1 - P_c)\right] \tag{9}$$

$$\frac{dP_c}{dt} = \frac{RT}{HP_T} \cdot \frac{(AK_c)}{V_c \cdot \rho \cdot n} \cdot P_c^{(1-n)}(P_1 - P_c) \tag{10}$$

Experimental

General Method. Two techniques, batch and flow, were used to study equilibria. The batch method was used to determine the adsorption of carbon dioxide, propane, and butane on wet-activated carbon at 1-atm. pressure. The equipment for the batch study is shown in Figure 1. The system was purged with the pure gas saturated with water vapor. Suspension from buret M, Figure 1, was added to the system and 1-atm. total pressure was maintained by allowing the gas, equal to suspension volume, to leave the system through stopcock N. Now gas-free suspension comes in contact with pure gas saturated with water vapor; the time of suspension introduction in the system is very short and can be neglected. The amount of gas sorbed was decided by the amount of mercury displaced in the reservoir flask to maintain constant pressure. When equilibrium is reached, pressure does not change any more. The amount absorbed by water can be calculated by using Henry's law and subtracted from the total volume sorbed to obtain the volume adsorbed on wet-activated carbon.

The solubilities in water (benzene, toluene, and trichloroethylene), the adsorption isotherm (CO_2), and the rates of transfer (all the compounds) were measured in a bubbler by the flow method. The equipment setup is shown in Figure 2. A known concentration of the pollutant was introduced into the bubbler at a constant flow rate and known total pressure. In general, low concentrations of vapors were used in this study. They varied from a few parts per million to a maximum of 3000 p.p.m. (for carbon dioxide) with the total pressure close to atmospheric. The concentration at the outlet was measured continually until, in the case of the equilibrium study, it reached about 99% of the inlet concentration. The results of the outlet concentration-transient allow the calculation of the sorption. The amount absorbed by the liquid can be deducted from the amount sorbed by the suspension to calculate the adsorption on wet adsorbent. Five 30-cc. bubblers were used in series for the adsorption isotherm experiments and a 500-cc. bubbler was used for the rest of the experiments. The five bubblers in series provided large contact areas and hence high efficiency, so that equilibrium was achieved rapidly and the limitations of the analytical instrument were overcome.

The method used for determining the adsorption isotherm of carbon dioxide requires special mention. The suspension was pretreated by bubbling air through it for 12 hours or more. This neutralized any basic groups present on carbon that may combine with carbon dioxide and provide added capacity above that of adsorption. Carbon dioxide concentration in the room was monitored to establish the base concentration. Experiments were performed in which pretreated suspension was stripped of carbon dioxide and then saturated with the room air to measure the adsorption capacity up to the carbon dioxide level of the room air.

Materials. Active carbon is the preferred adsorbent to remove organic vapors from air because of its selectivity for organic compounds. We selected the liquid phase application Nuchar C-190 as the adsorbent for most of the studies. Examination of Nuchar C-190 under the microscope indicated average particle size between 15 and 25 microns. Manufacturers of this carbon claim the surface area of 830 sq. meters per gram with most of the area (827 sq. meters per gram) in pore sizes larger than 20 A.

Two vapor-phase application carbons, BPL 120 × 30 and

BPL 28 × 48, were used only to compare the dry and the wet carbon adsorption capacities. Water was the logical choice as the inexpensive polar absorbent in combination with the nonpolar character of the adsorbent and the solute vapors. Some of the gases and vapors used in this study were carbon dioxide, methane, propane, butane, *n*-hexane, ethylene, trichloroethylene, acetone, butyl alcohol, amyl alcohol, benzene, and toluene. They cover a wide range of solubility and adsorption.

Gas Mixtures. Carbon dioxide, methane, and propane were obtained from the Matheson Co. as standard gas mixtures (background nitrogen) in the parts per million range and were 3000, 1000, and 104 p.p.m., respectively. All the other mixtures were prepared by the following method, except ethylene. Nitrogen from a nitrogen tank was bubbled through the organic liquid in a bubbler whose vapor mixture was to be prepared. The outlet from the bubbler, which is nitrogen carrying the vapor of the organic liquid, was fed to an evacuated gas tank. The amount of nitrogen bubbled was governed by the vapor pressure of the organic liquid at the room temperature and the concentration of the organic vapor desired in the final mixture. Now the bubbler containing organic liquid was removed from the line and the tank containing organic vapor was pressurized with nitrogen to about 50 p.s.i.g. This provided large enough volume of the mixture for the experiments. The ethylene mixture was prepared by directly feeding pure ethylene to the evacuated tank in the required amount and then following the above procedure.

Analytical Instruments. In all the experiments gas phase was analyzed. Carbon dioxide concentration was measured with the Infra Red Analyzer 215 of Beckman Instruments, Inc. It was calibrated by a standard 3000-p.p.m. carbon dioxide mixture (100% response) and nitrogen (0% response) before each experiment. IR215 response to concentration is not linear. The calibration curve for it was obtained from the company and checked. For all the organic gases and vapors total hydrocarbon analyzer Model 109 from Beckman Instruments, Inc., was used. The instrument was calibrated, before each experiment, with nitrogen (for null point) and a 104-p.p.m. standard propane mixture at constant flow rates of air, hydrogen fuel, and sample. The concentration of various organic mixtures was decided by comparison of the mixtures' response to that of 104-p.p.m. propane response, taking into account the effective carbon number of each compound.

The effective carbon number for a molecule was calculated from the effective carbon number for the atoms as given in the
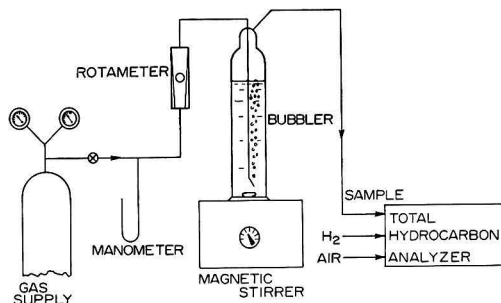
Figure 2. Experimental system for flow method
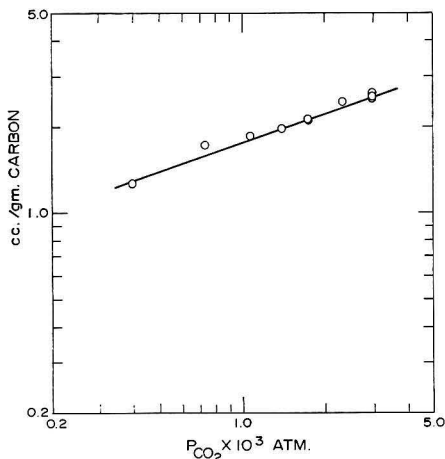
Figure 3. Adsorption isotherm of carbon dioxide on wet Nuchar C-190 at 25° C.
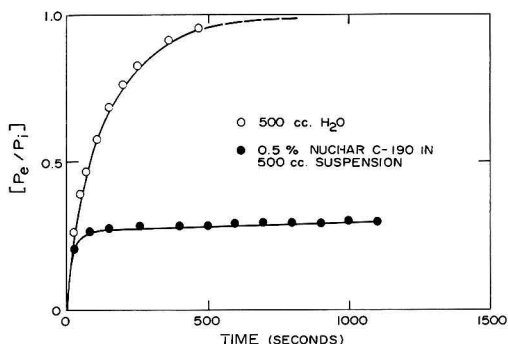
Figure 4. Unsteady-state sorption of trichloroethylene
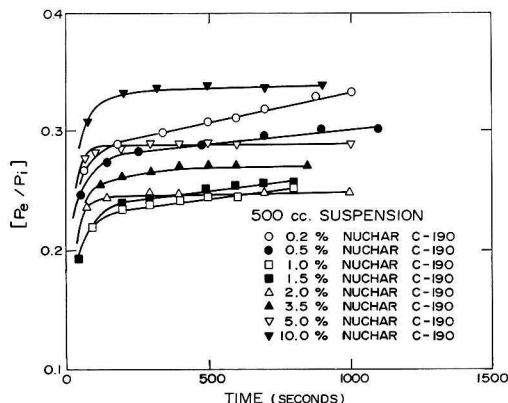
Figure 5. Effect of adsorbent concentration on sorption of trichloroethylene

instruction manual provided by Beckman Instruments, Inc., along with the total hydrocarbon analyzer, Model 109. The effective carbon numbers were empirically determined for various carbon and noncarbon atoms. The errors involved because of this in the calculation of concentration should be small.

Results and Discussion

Solubility. The knowledge of the solubility of the solute gas component in the liquid is essential to predict the intrinsic efficiency in the bubbler. Solubility data for some of the organics were experimentally determined, as they were not found in the literature. The solubilities were determined at only one concentration. Henry's law constant was calculated from the experimental results of the amount of vapor absorbed in water and its partial pressure in the gas phase. It is assumed that in the low concentration range, in which this work is carried out, Henry's law is valid.

Three runs were made in each case to check the reproducibility. Although the results were reproducible, they may have an error of as much as 5%, due to time lag, adsorption in the total hydrocarbon analyzer, and the empirical value of effective carbon number. The results are given in Table I.

Adsorption on Wet-Activated Carbon. Adsorption of carbon dioxide, propane, and butane was measured on wet-activated carbon at 1-atm. pressure, in the batch system. Two different types of carbon, BPL 12 × 30 and BPL 28 × 48, were used for carbon dioxide adsorption (Table II). Adsorption of carbon dioxide on dry carbon is taken from the literature for comparison of dry to wet capacity. Although the activated carbons are different, they allow a rough comparison. It can be seen from Table II that the results of this study and those of Munemori (1951) compare very well for carbon dioxide.

Comparison of the equilibrium data for propane and butane of this study with the adsorption on dry BPL 4 × 10 of Grant (1962), at 1-atm. partial pressure of the gases, shows that the wet carbon capacity is roughly 70% that of the dry carbon capacity for propane and the two capacities are roughly equal for butane. It is interesting to note that 6.5 cc. of propane and 2.0 cc. of butane absorb in 100 cc. of water and in contrast 68 cc. of propane or 140 cc. of butane adsorb on 1 gram of wet activated BPL 28 × 48, at 1-atm. partial pressure of the gases.

The adsorption at 1 atm. has given us some idea of the differences between adsorption on dry-activated carbon and wet-activated carbon, but the form of adsorption isotherm must be known before the equations for the rates of transfer to suspensions can be used. From the viewpoint of air pollution the interest was mainly centered on the adsorption isotherm in the low pressure range. Carbon dioxide was used in this study, although its adsorption is low, because it can be used for comparisons in the future work with a sieve plate column. Nuchar C-190 was the activated carbon as adsorbent.

Table I. Henry's Law Constants in Water at 25° C.

Vapor	Partial Pressure, Atm.	H, Atm./ (G. Moles/Cc.)
Benzene	103.2×10^{-6}	0.38×10^4
Toluene	58.4×10^{-6}	0.35×10^4
Trichloroethylene	202.5×10^{-6}	0.53×10^4

Table II. Adsorption on Dry- and Wet-Activated Carbon at 1-Atm. Partial Pressure of Gas and 30° C.

Gas	Carbon	Carbon Condition	Adsorption, Cc./Gram Carbon	% Capacity of Wet to Dry Carbon	Reference
CO_2	Columbia L	Dry	41.0	...	Ray and Box, 1950
CO_2	BPL 12 × 30	Wet	5.75	14.0	This study
CO_2	BPL 28 × 48	Wet	5.34	13.0	This study
Propane	BPL 28 × 48	Wet	68.2	...	This study
Butane	BPL 28 × 48	Wet	140.0	...	This study
CO_2	Kahlbaum's	Dry	33.5		Munemori, 1951
	charcoal	Wet	5.05	15.1	Munemori, 1951

The data are shown in Figure 3 on a log-log plot and seen to fall on a straight line. This is a Freundlich-type isotherm. It can be represented by the following equation:

$$V = ap^n$$

where $a = 145$ and $n = 0.693$.

Rates. In Figure 4 are given the results of the physical absorption and sorption of trichloroethylene. The ratio of the outlet to the inlet concentration is plotted against time as the abscissa. The over-all gas phase efficiency, $(P_i - P_e)/P_i$, of physical absorption in distilled water drops rapidly and approaches zero as the water becomes saturated. Whereas for sorption by a 500-cc. suspension of activated carbon (Nuchar C-190) in water, a high over-all gas phase efficiency is maintained, these curves appear to be starting from zero penetration, or 100% efficiency, because of dead volume of gas above the absorbing medium in the bubbler.

The effect of the concentration of activated carbon is shown in Figures 5 and 6. A pseudo-steady state is reached quickly in each case. The over-all gas phase efficiency varies little with time, once the initial dead volume effect is over. For low concentrations of activated carbon in suspension, where such peeudo-steady states are not achieved, the following discussion does not apply. If the straight lines are extended back to zero time, the intercept may be interpreted as representing an initial efficiency. This apparent initial efficiency (AIE) is defined as $(1 - P_e/P_i)$ at a time when the concentration gradient has just been established. At the AIE the concentration of the solute gas on the adsorbent is nearly zero and the concentration of
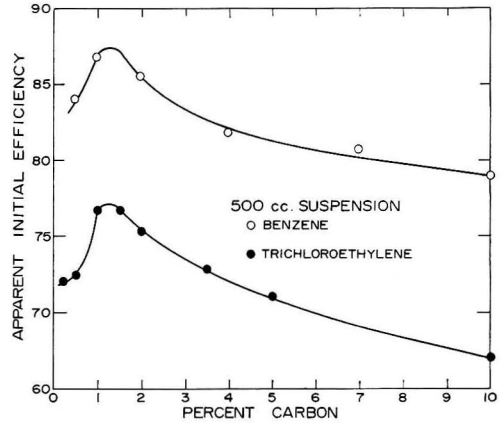
Figure 7. Effect of adsorbent concentration on apparent initial efficiency
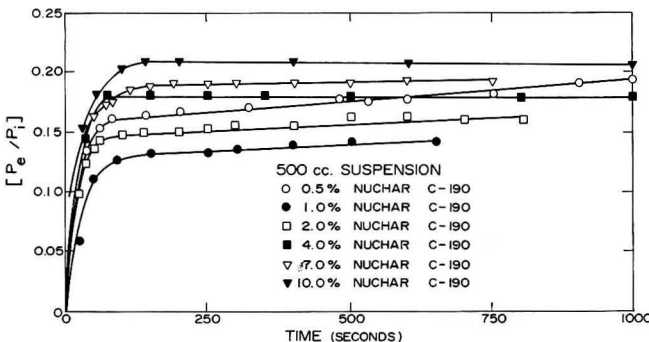
Figure 6. Effect of adsorbent concentration on sorption of benzene

the solute gas in the liquid is just enough to balance the rates of transfer from gas to liquid with that from liquid to solid.

The plots of AIE *vs.* the concentrations of the adsorbent for benzene and trichloroethylene are given in Figure 7. As the concentrations of the particles increase, the AIE increases, achieves a maximum at about 1 to 1.5% concentration, and then starts decreasing. According to Figure 4 P_e does not change with time during the initial period, excluding dead volume effect—i.e., $(dP_e/dt) = 0$. Then from Equation 8 $(dP_l/dt) = 0$ if $(dP_e/dt) = 0$. Also P_c is very nearly equal to zero. Hence Equation 9 can be simplified as follows:

$$P_e = P_i \left[1 - \frac{f}{1 + G \cdot f \cdot \frac{HP_T}{RTa} \frac{1}{AK_c}} \right] \quad (11)$$

Sufficiently high concentrations of particles in suspension will increase AK_c to the point where Equation 11 approaches $P_e = P_i[1 - f]$. This implies that the AIE approaches the intrinsic efficiency. It should be obvious from the definition of the AIE that higher the concentration of activated carbon the lower will be the concentration of the solute gas in the liquid and the AIE should approach the intrinsic efficiency. However, the maximum for the AIE is observed at about 1 to 1.5% concentration, after which it starts decreasing. The decrease may be due to hydrodynamic factors. Changed hydrodynamics will affect the bubble size distribution and the residence time distribution. These distributions directly affect the intrinsic efficiency of the bubbler for physical absorption. Hence, although the AIE may be very close to the intrinsic efficiency at high concentrations, it may decrease because of the changes in the intrinsic efficiency itself.

The rate data for the sorption of all the other organics were taken at 1% activated carbon concentration. This should allow us to find the AIE that is closest to the intrinsic efficiency of the bubbler for that organic compound. The intrinsic efficiency for physical absorption under the hydrodynamic conditions prevalent at 1% will differ from that at 0% concentration. But the concentration and the hydrodynamic factors are opposing and 1%, from Figure 7, still may be the optimum point to determine the AIE that would be closest to the intrinsic efficiency at 0%.

In Figure 8 are given the results of sorption for methane, propane, *n*-hexane, and ethylene. The physical absorption data
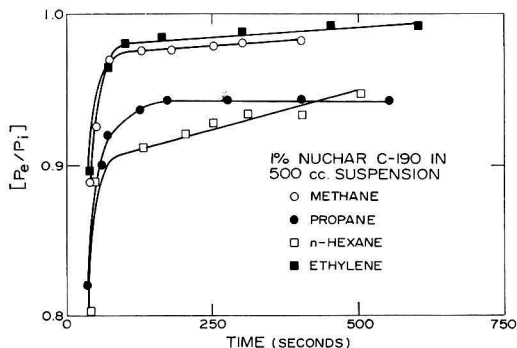
Figure 8. Sorption of hydrocarbon

for these hydrocarbons are not given, for except for the dead volume effect, the efficiency becomes zero too quickly to be measured. The results for physical absorption and sorption for toluene and amyl alcohol are shown in Figure 9. Butyl alcohol and acetone have very high solubility and 100% efficiency was obtained even for physical absorption in a 500-cc. bubbler.

A number of experiments were carried out to determine the intrinsic efficiency of the bubbler for physical absorption of carbon dioxide. Analysis of the results gave the value of $f = 0.31$. From Equation 4 we can see that changing the solute gas in the gas phase would change only the solubility constant, H, and the diffusivity, D. If the gases are sparingly soluble, we may say that the K_L has a square root dependence upon diffusivity. Hence,

$$f = 1 - e^{-\frac{0.371 (\sqrt{D}) 10^7}{H \times 1.57}} \quad (12)$$

Equation 12 can now be used to predict the intrinsic efficiency for the physical absorption of various organics. The prediction should have a good agreement with the experimental AIE, if our hypothesis about transfer mechanism is correct. Reliable data of solubility and diffusivity are, however, necessary to make meaningful predictions. Henry's law constants for propane and butane were calculated from solubility data (Seidell, 1941). The solubilities of benzene,

Table III. Experimental and Predicted Efficiency

Compound	H	D	Exptl. Efficiency (AIE), %	Predicted Efficiency, %
Carbon dioxide	2.7×10^4	1.77×10^{-5}	31	...
Methane	74.4×10^4	1.8×10^{-5}	2.0	1.35
Propane	36.6×10^4	1.0×10^{-5} A [a]	5.5	2.7
Butane	116.2×10^4	1.0×10^{-5} A	$\simeq 0$	0.8
n-Hexane	n.a.[b]	n.a.	10.0	...
Ethylene	20.5×10^4	1.59×10^{-5}	2.5	4.75
Benzene	0.38×10^4	1.0×10^{-5}A	87.0	86.2
Toluene	0.25×10^4	1.0×10^{-5}A	88.0	88.3
Trichloroethylene	0.53×10^4	1.0×10^{-5}A	76.8	75.8
Amyl alcohol	n.a.		74.0	...
Butyl alcohol	n.a.		100.0	...
Acetone	112.0	1.25×10^{-5}	100.0	100.0

[a] A = assumed.   [b] = n.a. not available.
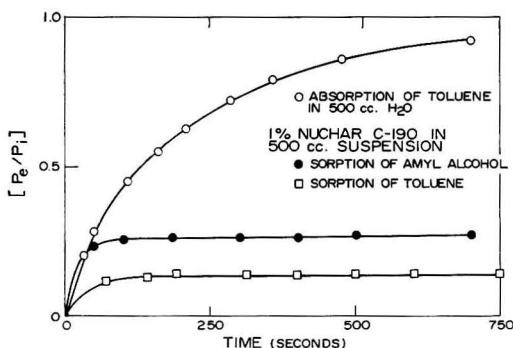
Figure 9. Sorption of toluene and amyl alcohol

toluene, and trichloroethylene were determined experimentally and the Henry's law constant for methane and ethylene was taken from Perry (1950). It is difficult to make reliable estimates of the diffusivity and where experimental diffusivity was not available it was taken as 1×10^{-5} sq. cm. per second. Table III summarizes the results.

The results in Table III show that the prediction of the intrinsic efficiency puts us in the right range of the experimental gas-phase efficiency. This leads us to an important conclusion that the solubility of the gas in liquid is the controlling factor for rates of transfer to suspensions. We cannot achieve the over-all gas-phase efficiency of sorption higher than the intrinsic efficiency of the system for physical absorption in the liquid under the same hydrodynamic conditions. The presence of high capacity adsorbent particles maintains a low concentration of the solute in liquid and, thus, keeps the efficiency close to the intrinsic efficiency.

Conclusions

The controlling factor for the rates of transfer to suspensions is the solubility of the solute gas in water. The results of the study suggest that the over-all gas-phase efficiency of the system for sorption by suspensions cannot be greater than the intrinsic efficiency of the system for physical absorption of the compound under the same hydrodynamic conditions.

The solubility of benzene, toluene, and trichloroethylene in water was determined at 25° C.

The absorption isotherm of carbon dioxide on wet Nuchar C-190 was determined in the range of 0 to 3×10^{-3} atm. at 25° C.

The absorption capacity of water can be increased to a great extent by addition of an adsorbent. In the presence of 2% (by weight) activated carbon, the capacity of water increases by 0.2 times for carbon dioxide, by 21 times for propane, and by 142 times for butane at 1-atm. pressure and 30° C.

The AIE (apparent initial efficiency) for sorption goes through a maximum with the increase of activated carbon concentration. The increase is explained by a mathematical model for the rates of transfer and the decrease is suggested to be due to hydrodynamic factors.

Suspensions would give a high over-all gas-phase efficiency in a practical contactor for compounds with high intrinsic efficiency for physical absorption.

Nomenclature

a = constant in Freundlich isotherm equation
A = area for transfer associated with liquid-carbon transfer
D = diffusivity of gas in liquid, sq. cm./sec.
f = intrinsic efficiency
G = flow rate of gas, cc./sec.
H = Henry's law constant
K_c = over-all mass transfer coefficient, liquid to solid
K_L = over-all mass transfer coefficient, gas to liquid, cm./sec.
k_L = liquid phase mass transfer coefficient
M_B = moles of gas in one bubble
n = constant in Freundlich isotherm equation
N_A = rate of transfer, gram moles/sec.
P_i = partial pressure of solute gas in inlet to bubbler, atm.
P_e = partial pressure of solute gas in exit from bubbler, atm.
P_1 = partial pressure of solute gas, atm., in equilibrium with concentration of solute gas in liquid
P_c = partial pressure of solute gas, atm., in equilibrium with concentration of solute gas on wet-activated carbon
P = partial pressure of solute gas in gas phase, atm.
P_T = total pressure of gas
r = radius of bubble
R = gas law constant
t = time, sec.
t_r = average residence time of a bubble in liquid
T = temperature, ° K.
U_B = bubble rise velocity, cm./sec.
V, V_1, V_c = volume of gas adsorbed, volume of liquid, volume of solid, cc.
w = grams of carbon in liquid

Greek

ρ = density of carbon

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Adsorption of Selected Pesticides on Activated Carbon and Mineral Surfaces

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■ The clay minerals illite, kaolinite, and montmorillonite suspended in dilute pesticide solutions adsorb very little 2,4-dichlorophenoxyacetic acid (2,4-D) or isopropyl N-(3-chlorophenyl) carbamate (CIPC). Adsorption of CIPC from aqueous solution with powdered activated carbon is extensive. Equilibrium conditions for the CIPC-activated carbon system can be represented by a Freundlich isotherm. Physical or weak chemical bonding between the CIPC and the carbon surface is suggested. There is some indication that this particular adsorption process is diffusion-controlled.

T he presence of pesticides in drinking water supplies is becoming a problem of increasing magnitude. Because of their highly toxic nature, these compounds are a potential hazard to man's health and well being. As yet, there is very little information available concerning the physical, chemical, and biological factors affecting the persistence of these toxic chemicals in water.

These studies were undertaken with two purposes in mind. First, to ascertain the ability of certain clay minerals to adsorb pesticides from solution. Related substances are found in many natural river and stream systems. If pesticides are adsorbed on such matter in relatively large quantities, their subsequent removal at water-treatment plants might be facilitated. Coagulation, sedimentation, and filtration would remove the par-

ticulate matter from the water. More directly, the adsorption of pesticides on clay minerals might result in the deposition of the chemicals in bottom muds.

The second purpose was to investigate the removal of one class of pesticides, the carbamates, from water with powdered activated carbon. Previous studies on the removal of pesticides from water supplies have indicated that adsorption on activated carbon is the most effective. The earlier studies encompassed a variety of chlorinated hydrocarbon and organic phosphorus pesticides, but not the carbamate compounds.

The pesticides selected for these experimental studies were isopropyl N-(3-chlorophenyl) carbamate (CIPC) and 2,4-dichlorophenoxyacetic acid (2,4-D). Both compounds are herbicides widely used in agricultural operations. 2,4-D is one of a number of chlorinated hydrocarbon pesticides that have been isolated from drinking water supplies.
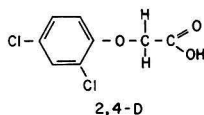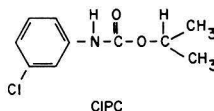
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2,4-D

2,4-DICHLOROPHENOXYACETIC ACID

CIPC

ISOPROPYL N-(3-CHLOROPHENYL) CARBAMATE
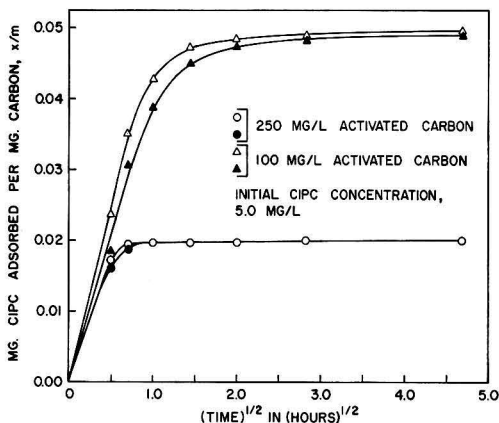
Figure 1. CIPC adsorbed per unit weight of activated carbon 100 and 250 mg. per liter at pH 6.9 and 20° C.
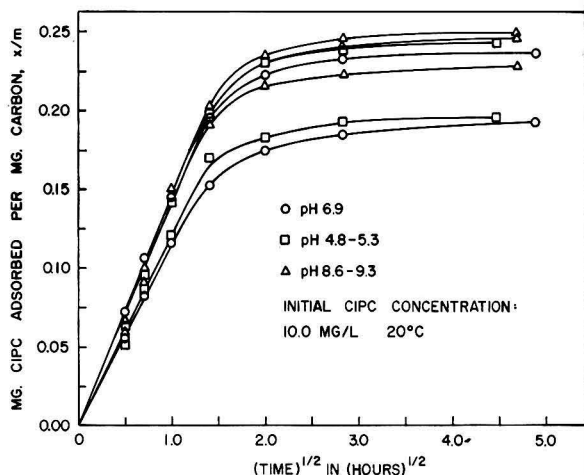
Figure 2. Adsorption of CIPC on 25 mg. per liter of activated carbon for different pH values

Table I. Adsorption of CIPC and 2,4-D on Clay Minerals

Pesticide		Clay Minerals			Elapsed Time, Hr.	Pesticide Remaining in Solution, %
Compound	Concn., mg./l.	Type	Concn., mg./l.	pH		
CIPC	0.40	Montmorillonite	50	6.9	47	96.5
			100	6.9	47	96.8
			200	6.9	47	96.8
			400	6.9	47	96.0
			800	6.9	47	96.0
				4.8	23	97.2
				9.3	23	96.6
		Illite	800	6.9	21	96.0
				4.8	21	96.3
				9.3	21	97.3
	0.40	Kaolinite	800	6.9	21	96.7
				4.8	21	96.4
				9.3	21	97.0
2,4-D	0.13	Montmorillonite	800	6.9	23	99.1
				4.8	23	99.8
				9.3	23	99.9

Experimental Materials

Radioactively labeled CIPC and 2,4-D were used in these adsorption studies in order to obtain accurate and rapid measurements at relatively low pesticide concentrations. Both pesticides contained carbon-14 atoms in their molecular structure. Experiments were performed at three pH values: 4.8, 6.9, and 9.3. Appropriate concentrations of sodium phosphate (mono- and dibasic) and sodium borate were employed to maintain the pH at the desired values. The water used in the experiments was double-distilled. Powdered activated carbon (West Virginia Pulp and Paper Co., Nuchar C-190) and the clay minerals illite, kaolinite, and montmorillonite were used as adsorbents. For the activated carbon, the diameter of the median particle was 1.65 microns, with a geometric standard deviation of 2.27. To ensure maximum wetting, the carbon was added from a stock suspension.

Experimental Procedures

The adsorption experiments were normally conducted in 1-liter beakers containing 800 ml. of test solution. Suspensions of the pesticide and adsorbent were placed on a multiple stirring apparatus operated at 100 r.p.m. Periodically, samples were taken and the amount of pesticide remaining in solution was determined. For experiments with the clay minerals, the samples were centrifuged to separate the liquid and solid phases. In order to obtain the rapid phase separation required in the studies with activated carbon, the samples were filtered through porous stainless steel immersion tubes. The aqueous solutions were then dissolved in a *p*-dioxane counting fluor and assayed with a liquid scintillation counting system.

A series of experiments to determine the total capacity of the activated carbon for CIPC differed slightly from the experiments described above. In this instance, the test vessels were 2-liter beakers initially containing 1800 ml. of solution. Additional quantities of CIPC were added at 24-hour intervals.

Results

Adsorption on Clay Minerals. The adsorption of CIPC on illite, kaolinite, and montmorillonite was studied at pH values of 4.8, 6.9, and 9.3. Initial pesticide concentrations of 0.04 mg. per liter were employed for clay mineral concentrations of 50 to 800 mg. per liter. The results of these experiments are summarized in Table I. Adsorption of CIPC amounted to 4.0% or less in all the experiments for contact periods up to 47 hours. Table I also contains the data from an experimental series performed on the adsorption of 2,4-D on montmorillonite. After 23 hours, less than 1% of an initial 2,4-D concentration of 0.13 mg. per liter had disappeared from solution.

Adsorption on Activated Carbon. The studies with activated carbon were confined to CIPC. For the first experimental series, the CIPC concentration was 5.0 mg. per liter and the activated carbon concentrations were 100 and 250 mg. per liter. Data collected from this experiment are presented in Figure 1. More than 95% of the CIPC was adsorbed on the carbon within 4 hours. Subsequent experiments were performed with an adsorbate concentration of 10.0 mg. per liter and adsorbent concentrations of 25 and 50 mg. per liter.

To study the effects of pH on the adsorption process, three sets of experiments were conducted at 20° C. for pH values of 4.8, 6.9, and 9.3. The results of these experiments, corrected for small pesticide losses observed in control blanks and for evaporation, are presented in Figures 2 and 3. The pH of the systems changed slightly during the experiments. It is apparent that the results varied somewhat between duplicate samples, especially for an activated carbon concentration of 25 mg. per
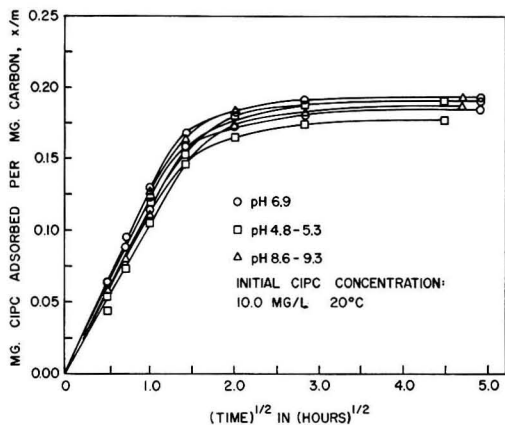
Figure 3. Adsorption of ClPC on 50 mg. per liter of activated carbon for different pH values

Figure 4. Adsorption of CIPC on 25 mg. per liter of activated carbon at 20° and 37° C.

liter. These differences are attributed to unequal carbon concentrations arising from the retention of small amounts of carbon on the surfaces of the experimental apparatus, transfer pipets, and sampling equipment. Such differences would be most apparent at the lower activated carbon concentration.

One series of experiments was conducted at 37° C. and a pH of 6.9. Data collected during this series are given in Figures 4 and 5, along with the corresponding results for 20° C. A separate study was made to measure the adsorption capacity of activated carbon for CIPC. This study was of 5 days' duration and the results are presented in Figure 6. Additional quantities of CIPC were added after 24, 48, and 73 hours had elapsed. Only nonradioactive CIPC was used for the 73-hour addition, resulting in a decrease in the over-all ratio of radioactive to nonradioactive CIPC. The treatment of the data collected during the 73- to 128-hour time interval is discussed below.

Discussion

Adsorption on Clay Minerals. The general impression given by the results of these investigations is that, at most, only a small percentage of any CIPC or 2,4-D present in a natural waterway will be removed on suspended clay minerals or related particulate matter. The 800 mg. per liter clay concentration employed in these studies is representative of a river with a high suspended-solids content. In the CIPC experiments, maximum removals ranged from 3.0 to 4.0%. Control systems devoid of adsorbent, however, indicated that even these small reductions may have resulted primarily from volatilization or adsorption on the experimental equipment. The disappearance of 2,4-D from solution in no instance amounted to more than 1%. Extrapolation of the results of Aly and Faust (1964) concerning the adsorption of 2,4-D on bentonite indicates agreement with the present study.

Adsorption on Activated Carbon. Significant quantities of CIPC are absorbed from solution by powdered activated carbon. At pH 6.9 and 20° C., initial CIPC concentrations of 5.0 mg. per liter were reduced by more than 90% within 2 hours and 98% within 22 hours with 100 mg. per liter of activated carbon. Under similar conditions, 25 and 50 mg.
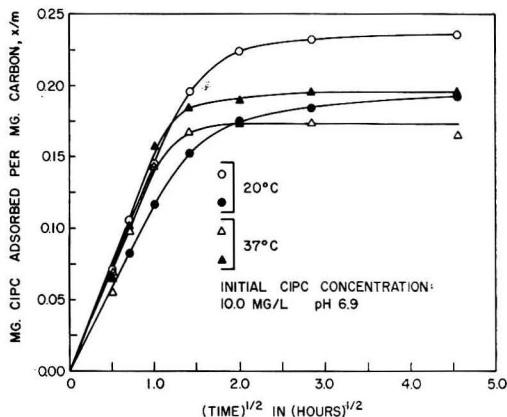
per liter of carbon removed about 56 and 95%, respectively, of the CIPC, initially present at 10.0 mg. per liter, within 24 hours. It is evident from the data that equilibrium is closely approached within 20 to 24 hours of contact. Approximately 90% of the adsorption occurs within the first 4 hours.

ADSORPTION CAPACITY. Results from the capacity experiments show that after three equilibrium periods the total adsorption capacity of the activated carbon had not been exhausted. It was, however, being approached when the values of x/m—i.e., milligrams of CIPC adsorbed per milligram of carbon—ranged from 0.291 to 0.334 after 73 hours.

The final addition of CIPC contained no radioactively labeled pesticide. The ratio of radioactive to nonradioactive species in the previous additions had been maintained at the value established initially. Immediately after the final addition, therefore, the ratio of radioactive to nonradioactive CIPC molecules in solution was significantly decreased. Thus, the data collected during the 73- to 128-hour time interval reflect not only the progression to a new chemical equilibrium, but also any redistribution of the radioactivity that may have occurred.

The results of the final equilibrium period can be examined in terms of the two extremes for radioactivity redistribution as shown in Figure 6. First, complete redistribution of the radioactivity is assumed to have occurred within a very short time after the CIPC addition. On this basis, the increases in the amounts of CIPC adsorbed are much larger than the incremental changes observed in the previous equilibrium interval. The indications are that, while chemical equilibrium probably had been obtained, redistribution of the radioactivity was not complete after 55 hours. The other extreme can be examined by assuming that no redistribution of radioactivity occurred between the solid and liquid phases. In essence, the adsorption of CIPC is assumed to be irreversible. The evaluation of the data with respect to the above assumption gives rise to the apparent initial desorption of CIPC. Obviously this apparent desorption is inconsistent with the assumption of adsorption irreversibility.

It can be concluded from these two interpretations of the data that redistribution of the radioactive CIPC molecules
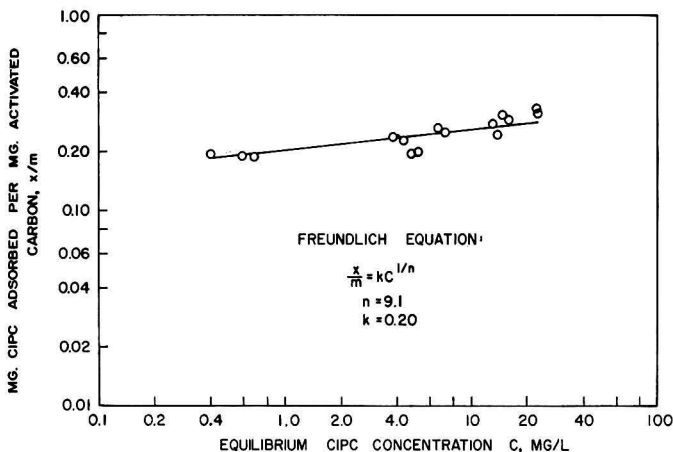
Figure 7. Freundlich isotherm for adsorption of CIPC on activated carbon at pH 6.9 and 20° C.
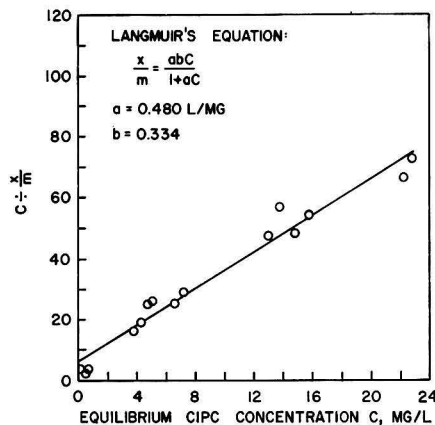
Figure 8. Langmuir isotherm for adsorption of CIPC on activated carbon at pH 6.9 and 20° C.

between the solid and liquid phases did take place. This redistribution, however, occurred rather slowly and was not complete even after 55 hours. Increased levels of radioactivity in the bulk solution gave conclusive evidence of the reversibility of this particular adsorption process. Such reversibility is typical of physical adsorption as opposed to chemisorption.

ADSORPTION ISOTHERMS. By using the data from all of the studies conducted at pH 6.9 and 20° C., Freundlich and Langmuir adsorption isotherms can be constructed as shown in Figures 7 and 8. The conditions that existed after 24 hours were assumed to represent equilibrium. While this assumption may not be strictly valid, certainly equilibrium conditions were closely approached after 24 hours of contact. Although a small amount of scatter is noticeable, good correlations between the data and both the Freundlich and Langmuir expressions are obtained. In the Langmuir equation, the value of b represents the theoretical capacity of the adsorbent for the particular adsorbate, since the value of x/m approaches b as concentration C approaches infinity. A theoretical capacity of 0.334 mg. of CIPC per mg. of activated carbon is indicated for the current investigation. This value agrees with the values obtained in the actual capacity studies. Information from those investigations showed that the capacity was being approached when the x/m values ranged from 0.291 to 0.334 after three equilibrium periods.

Table II. Amounts of Activated Carbon Required to Reduce CIPC Concentrations to Acceptable Levels within 24 Hours

CIPC Concn., Mg./L.		Concn. of Activated Carbon Required, Mg./L.	
Initial	Desired final	Freundlich isotherm	Langmuir isotherm
5.0	1.0	20.0	37.0
5.0	0.5	24.3	69.5
3.0	0.5	13.5	38.8
1.0	0.5	2.7	7.7
1.0	0.1	6.0	59.0
0.5	0.1	2.7	26.2

The Freundlich and Langmuir isotherms provide a convenient method for estimating the amount of activated carbon necessary to reduce the concentration of CIPC to a particular level at equilibrium. Table II contains the results of such computations for different initial concentrations of CIPC. The values presented in Table II represent equilibrium conditions attained after approximately 24 hours of contact. Previously cited results, however, showed that equilibrium values were closely approached after 4 hours. Calculations based on these isotherms, therefore, may be considered approximately valid for 4-hour contact periods.

Obvious discrepancies exist between the amounts of carbon required for a given CIPC removal computed with the Freundlich equation and the same values based on the Langmuir equation. At low equilibrium concentrations, the Langmuir isotherm appears to fit the data poorly. The experimental data obtained for CIPC equilibrium concentrations less than 1.0 mg. per liter lie below the Langmuir isotherm. At these concentrations, the adsorption is considerably greater than that indicated by the isotherm. While the Langmuir expression may be considered to apply to a wide range of equilibrium concentrations, its validity at low pesticide concentrations for the activated carbon–CIPC system is questionable. The Freundlich isotherm appears to represent the actual adsorption equilibrium more closely for low equilibrium concentrations of CIPC.

pH EFFECTS. Previous studies on the adsorption of organic compounds on activated carbon have indicated a definite effect of pH on the adsorption rates. Weber and Morris (1963a) found that the rate of adsorption of alkylbenzenesulfonates was faster at low pH values. These authors attributed this pH dependency to changes in the surface characteristics of the adsorbent. Schwartz (1962) observed that high hydrogen ion concentrations increased the rate of uptake of 2,4-D from solution. Both of these studies dealt with anionic species. An increase in the hydrogen ion concentration would tend to reduce the repulsive forces between the anionic compounds and the activated carbon, thus enhancing the rate of adsorption.

An examination of the molecular structure of CIPC indicates that it would have little tendency to ionize in aqueous

Figure 5. Adsorption of CIPC on 50 mg. per liter of
activated carbon at 20° and 37° C.

Figure 6. Adsorption capacity studies

Milligrams of CIPC adsorbed per unit weight of activated carbon at pH 6.9, 20°C

solution. At low pH, some protonation of the amino group
might be observed. The acidity constant of the acid form of
CIPC is estimated to be on the order of 10^{-5}. At pH values of
6.9 and 9.3, the compound would be expected to exist almost
entirely in the molecular form as opposed to the ionic species.
Appreciable quantities of the protonated molecule might exist
only at pH 4.8.

The results of the studies on the effects of pH on the adsorp-
tion of CIPC produced significant differences between dupli-
cate systems. These differences were attributed previously to
retention of unequal quantities of adsorbent on the surfaces of
the experimental containers and apparatus. In spite of these
variations, the results are of value in assessing the effects of
pH on adsorption. Attention should be focused on those sys-
tems in each of the three pH ranges that demonstrated the
largest amounts of adsorption. Only small differences, of little
or no significance, were observed in the total amount of CIPC
adsorbed. Moreover, the initial adsorption rates did not ex-
hibit any effects attributable to pH changes for either of the
adsorbent concentrations.

Over the pH range of 4.8 to 9.3, it can be concluded that the
total amount and rate of adsorption of CIPC on activated
carbon remain essentially constant. Any changes that may
occur in the character of the carbon surfaces over this pH
range, therefore, do not affect the adsorption of CIPC. The
preceding statement by no means excludes the possibility that
the hydrogen ion concentration influences the nature of the
adsorbent surfaces. Indeed, alterations in the electrokinetic
nature of the surfaces would be anticipated.

TEMPERATURE EFFECTS. From the adsorption studies at 20°
and 37° C., it is evident that the initial adsorption rates for
CIPC were faster at the higher temperature. On the other hand,
the total amounts of pesticide adsorbed were greater at 20° C.
The information obtained in these studies can be used to esti-
mate the heat of reaction and the activation energy for the
adsorption of CIPC on activated carbon. The heat of reaction
is related to the equilibrium constant by the van't Hoff equa-
tion, which, over small temperature ranges, can be expressed
as:
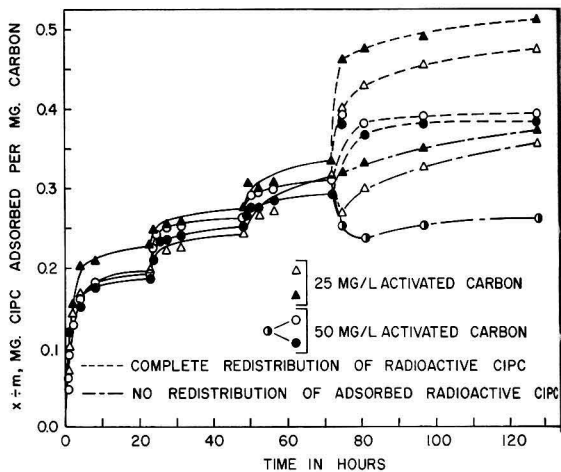
$$\ln \frac{K_2}{K_1} = \frac{\Delta H(T_2 - T_1)}{R T_1 T_2}$$

where K is the equilibrium constant, T is the absolute tempera-
ture, ΔH is the heat of reaction, and R is the gas constant.

To calculate the equilibrium constant, the following reaction
model was selected:

$$P + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} PC$$
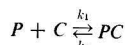
where P is the pesticide, C is the activated carbon, PC is the
adsorbed pesticide–carbon complex, and k_1 and k_2 are reaction
rate constants. The equilibrium constant, K, can be expressed
as:

$$K = \frac{(PC)}{(P_o - PC)(C_o - PC)}$$

where PC is the amount of pesticide adsorbed per unit volume,
P_o is the initial pesticide concentration, and C_o is the concen-
tration of activated carbon adsorption sites. C_o can be ex-
pressed in terms of the capacity of the carbon for the pesticide.
For the activated carbon–CIPC system, the value of 0.334
mg. of CIPC per mg. of carbon is employed.

For the adsorbent concentrations of 25 mg. per liter, the
heat of reaction is computed to be -6.1 kcal. per mole based
on the average values of the equilibrium constant, K. If, in-
stead, the values for K for the systems in which the maximum
adsorption occurred at each temperature are used in the cal-
culation, the heat of reaction is found to be -7.3 kcal. per
mole. For the activated carbon–CIPC system, therefore, the
heat of reaction is about -7.0 kcal. per mole.

The heat of reaction in part reflects the energies of the bonds
broken and formed during the reaction. For typical adsorption
processes, the energy of the adsorption bond is of the same
order of magnitude as the heat of reaction. In some instances,
these two quantities may be almost identical. The heat of
reaction for the adsorption of CIPC on carbon is low, indi-
cating physical or weak chemical bonding. For this system,
hydrogen bonding might exist between the amino hydrogen
atom of the CIPC molecule and carbonyl oxygen atoms exist-

ing on the carbon surface. This type of bonding is of importance in protein chains. While the actual bonding mechanism cannot be established, it can be concluded that some type of physical or weak chemical bonding exists between the CIPC and the activated carbon.

A relationship similar to the van't Hoff equation exists between the activation energy and the rate of reaction. This expression developed by Arrhenius is:

$$\ln \frac{k_2}{k_1} = \frac{E_a(T_2 - T_1)}{RT_1T_2}$$

where k is a reaction rate constant, T is the absolute temperature, E_a is the activation energy, and R is the gas constant. The linear initial portions of the adsorption curves can be used to calculate the initial rate constants. Using the average values for these constants, the activation energy is calculated to be 3.4 kcal. per mole.

ADSORPTION KINETICS. The kinetics of the adsorption of organic compounds on activated carbon in an aqueous medium are not fully understood. Recently Weber and Morris (1963a, 1963b, 1964) have postulated that intraparticle diffusion is the controlling step in the adsorption of certain organic substances on carbon. The adsorption of organic substances on activated carbon in a turbulent system involves several processes. It consists of the transfer of molecules to the laminar boundary layer surrounding each adsorbent particle, diffusion through the boundary layer to the carbon surface, reaction or adsorption on the surface, and diffusion into the complex matrix of the particle. If the rate-controlling step is substantially slower than the other three processes, the over-all rate of adsorption may be represented by the mathematical formulation for the controlling process.

Attempts were made to correlate the experimental data from the present study with a number of theoretical reaction and diffusion models. Among the models examined were: the adsorption at the surface represented as a second-order reversible reaction; diffusion to the carbon surface with the surface conditions represented by Langmuir's equation; and diffusion from solutions of limited volume into spheres, cylinders, and planes in well mixed systems.

One of the most striking features of the adsorption data is the linear relationship between the amount of CIPC adsorbed and the square root of time during the initial periods of the experiments. Previously, this relationship was employed to compare initial adsorption rates. The linear dependency was followed for about the first hour of the studies. Mathematical models for many different diffusion processes predict the same dependency for the initial periods. Among the systems demonstrating this feature are the diffusion from solutions of limited volume into various geometrical bodies in stirred solutions and the diffusion to a hollow sphere from a concentric surface maintained at constant concentration. Numerous examples of this relationship between the amount of material transferred to a surface and $t^{1/2}$ are presented by Crank (1956). While the experimental data did not fit any mathematical model of adsorption kinetics examined, the adsorption curves are similar to those for many diffusion-controlled sorption processes.

Conclusions

The studies on the adsorption of selected pesticides on activated carbon and clay mineral surfaces can be summarized in the following statements.

Clay minerals suspended in dilute pesticide solutions adsorb very little 2,4-D and CIPC. At most, only 1% of an initial 2,4-D concentration of 0.13 mg. per liter was adsorbed within 23 hours on 800 mg. per liter of montmorillonite. Illite, kaolinite, and montmorillonite at concentrations as high as 800 mg. per liter adsorbed no more than 4% in 24 hours of the CIPC initially present at a concentration of 0.40 mg. per liter. No effects of hydrogen ion concentration were discernible.

Powdered activated carbon readily adsorbs CIPC from aqueous solutions. In the well stirred experimental systems, approximately 24 hours were required to reach equilibrium. Of the total equilibrium adsorption achieved in 24 hours, about 90% was attained in 4 hours. The adsorption equilibrium of the activated carbon–CIPC aqueous system can be represented closely by a Freundlich isotherm. For the Freundlich expression, $x/m = kC^{1/n}$, constants n and k were calculated to be 9.1 and 0.20, respectively. The ultimate capacity of the activated carbon for CIPC is estimated to be about 0.34 mg. of CIPC per mg. of carbon.

The adsorption of CIPC on activated carbon is independent of the hydrogen ion concentration over the pH range from 4.8 to 9.3. With an estimated acidity constant of about 10^{-5}, CIPC would exist predominantly in the molecular form over most of the experimental pH range.

The adsorption of CIPC on activated carbon appears to involve physical or weak chemical bonding. The heat of adsorption is estimated to be -7.0 kcal. per mole. Adsorption processes involving electrostatic or weak chemical bonds typically have heats of adsorption of the same order of magnitude. Furthermore, the adsorption of CIPC is reversible. Such reversibility is an additional indication of physical or weak chemical bonding. The structure of CIPC would seem to be well suited for hydrogen bonding between the amino group and carbonyl oxygen atoms on the activated carbon surface.

Initial rates of adsorption for the CIPC–activated carbon system vary directly with the square root of time. This relationship is characteristic of many diffusion-controlled sorption processes. The nominal activation energy is estimated to be about 3.4 kcal. per mole, a value indicative of diffusion-controlled processes.

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COMMUNICATIONS

Selenium in the Atmosphere

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■ Selenium was determined by neutron activation in 22 samples of snow and rain collected during the 1964–1965 winter and in seven air samples collected during the following spring in Cambridge, Mass. Sulfate was determined gravimetrically or turbidimetrically in most of the samples. In these samples and in well water and Cambridge tap water analyzed for comparison, the selenium concentration averaged 0.2 μg. per liter of water or per 200 cu. meters of air, and the average value of the weight ratio Se/S = 1×10^{-4}. Approximately the same ratio is commonly found in igneous and sedimentary rocks, sulfide ores, and fossil fuels, but the sea water ratio is one thousandth as large. This information implies mainly a terrestrial, including pollution, source for selenium as well as sulfur in the atmosphere of the city of Cambridge.

The very rapidly growing literature on sulfur in the atmosphere (Junge, 1963) reflects its importance, both as a hazardous pollutant and as a significant natural component. In contrast, the literature on atmospheric selenium (Gassman, 1918; Suzuki, 1959) is very sparse, although its toxicity has been recognized (Cerwenka and Cooper, 1961). In geochemical studies of trace substances there is considerable value in measuring the concentrations of closely related elements, for differences in abundances may be interpreted quantitatively in terms of their slightly different, and often well understood, chemical properties. Stable isotopic abundance measurements have been especially successful and have revealed details of geochemical processes in the atmosphere, hydrosphere, and lithosphere which could not be seen by measurements of single elements. Different elements with similar properties can be studied in the same way, and the halogen components of sea salt have already been extensively investigated (Winchester and Duce, 1967). A study of the element pair sulfur and selenium may reveal more about the atmospheric behavior of both elements than a study of either

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element alone. This paper is a report of our first determinations of atmospheric selenium.

Experimental

Classical determination of Se by precipitation and turbidimetry (Robinson *et al.*, 1934) is sensitive only to 10 μg. and is not suitable for the present investigation. Colorimetric determination by 3,3'-diaminobenzidine (Hoste, 1952; Cheng, 1956; Dye, *et al.*, 1963) and determination by neutron activation (Bowen and Cawse, 1963) both offer much greater sensitivity, and activation analysis offers possibility of chemical yield control during analysis by radioactivity measurement. The greatest neutron activation analysis sensitivity is obtained by measuring 17.5-second Se^{77m}, but the short half life demands special equipment not available to us. High sensitivity is also obtained by measuring 18.6-minute Se^{81}, but interference by radioactivity of 18-minute Br^{80} makes its measurement difficult. Adequate sensitivity is obtained after several hours of irradiation by measurement of 120-day Se^{75}, and 0.01 μg. of Se is a practical sensitivity limit when gamma radiation is measured with a scintillation spectrometer. The long half life permits the analysis of a large number of samples and standards in a single neutron irradiation.

Approximately 1 liter of rain or snow melt water was collected on polyethylene, filtered on filter paper to remove soot, acidified with HNO_3, evaporated to 20 ml. at 40 millibars and 50° C. in an evacuated flash evaporator, and reduced to 0.1 ml. in a Teflon beaker by gentle heating in a dust-free enclosure. Tests were made of the procedure using carrier-free 120-day Se^{75} tracer (Hashimoto and Winchester, 1967) to select conditions such that no Se would be lost in these steps. The samples were then transferred to quartz ampoules for neutron irradiation. Air samples of approximately 100 cu. meters were taken by passing air at about 1 cu. meter per hour either through an aqueous bubbler or through a 1-micron pore diameter Millipore filter. The aqueous solutions were processed in the same way for irradiation, but the Millipore filters were irradiated directly without processing.

Neutron irradiations of up to 14 hours were carried out in the MIT reactor at a flux of approximately 2×10^{13} n/sq. cm. sec. in the vertical facility. Three samples and standard solutions sealed in quartz were contained in each of eight aluminum vials arranged lengthwise in the reactor, and small differences in neutron flux over the irradiation region were accounted for by the arrangement of the standards. Three weeks

after irradiation, Se was distilled from HCl + HBr solution by passing in Br_2 vapor, and halogens were expelled from the distillate by evaporating in a Teflon beaker in the presence of HNO_3 to 1-ml. volume. Precipitation of the activity with mixed Se(IV) and Te(VI) carriers was accomplished by first ensuring chemical exchange by oxidation with HNO_3 and H_2O_2 in the presence of HBr and then by reducing to the elemental form by hydrazine in HCl. The precipitate was coagulated by heating, filtered on glass fiber filter paper, dried, and transferred to a vial for gamma counting in a NaI(Tl) well-type scintillation counter and a TMC 400-channel analyzer. Characteristic 0.138-, 0.410-, and 0.265 + 0.280 + 0.305-m.e.v. gamma-ray photopeaks provided an easy identification of Se^{75} radioactivity. The integrated sum of these three peaks, after background subtraction, was calculated for each sample and standard, and Se contents were computed assuming that radioactivity is directly proportional to the amount of Se present. All samples were recounted approximately 6 months later, and the radioactivity levels had decreased by the amount expected from the half life of 120-day Se^{75}.

Most of the samples were also analyzed for sulfur using ASTM gravimetric or turbidimetric determination of $BaSO_4$ (ASTM Standards, 1964). Although we consider these results to be less precise than the neutron activation determination of Se, they are consistent with the literature (Junge, 1963) and are useful for comparative purposes.

Results and Discussion

The analytical results are given in Table I. Most of the precipitation and all of the air samples were collected on the MIT campus located in the middle of the city of Cambridge near Boston. There appears to be no significant difference between Se and S in samples at ground level and on the roof of the 90-meter high earth science building nor between these and samples taken at other points in Cambridge. However, samples taken in semirural Topsfield and Boxford and in the smaller city of New Haven suggest that Se concentration is lower in these areas.

The average value of the Cambridge precipitation samples is 0.21 μg. of Se per liter and 2.0 mg. of S per liter, making the average weight ratio Se/S = 1×10^{-4}. In the two Cambridge air samples where sulfur determinations were made, about the same ratio was found, and the concentrations indicate that 1 liter of precipitation is roughly equivalent to 200 cu. meters of air.

Table I. Atmospheric Se and S Concentrations

Location	Date, 1964–65	Se, μg.[a]	S, mg.[a]	Se/S $\times 10^4$	Remarks
1	Dec. 18	0.15	. . .	. . .	Falling snow
2	Dec. 18	0.09	3.9	0.2	Falling snow
1	Jan. 3	1.40[b]	0.5[b]	. . .	Rain + ice
2	Jan. 3	0.70	2.5	2.8	Rain + ice
1	Jan. 10	0.13	. . .	. . .	Falling snow
2	Jan. 10	0.16	3.8	0.4	Falling snow
1	Jan. 16	0.53	1.2	4.4	Falling snow
2	Jan. 16	0.52	1.4	3.7	Falling snow
1	Jan. 24	0.14	2.7	0.5	Falling snow
2	Jan. 24	0.16	1.3	1.2	Falling snow
3	Feb. 22	0.25	2.3	1.1	Falling snow
2	Feb. 25	0.10	2.7	0.4	Rain
3	March 20	0.08	0.9	0.9	Ground snow
2	March 20	0.06	0.9	0.7	Falling snow
3	March 29	0.10	1.5	0.7	Ground snow
1	March 29	0.09	1.4	0.6	Falling snow
2	March 29	0.10	1.2	0.8	Falling snow
Mean		0.21	2.0		
4	Jan. 31	0.08	1.5	0.5	Ground snow
5	Feb. 27	0.03	2.4	0.1	Ground snow
5	March 20	0.12	0.5	2.4	Ground snow
6	March 20	0.04	0.7	0.6	Ground snow
6	March 20	0.10	1.5	0.7	Ground snow
1	. . .	0.11	1.7	0.7	Tap water
5	Feb. 27	0.09	2.0	0.5	Well water
1	May 11	0.03	. . .	. . .	Air, bubbler
1	May 20	0.03	. . .	. . .	Air, bubbler
1	May 20	0.11	. . .	. . .	Air, filter
1	May 27	0.13	0.97	1.4	Air, bubbler
1	May 27	0.16	. . .	. . .	Air, filter
1	June 1	0.06	0.69	0.9	Air, bubbler
1	June 1	0.10	. . .	. . .	Air, filter

Sampling locations. 1. MIT campus roof of earth science building. 2. Ground location near 1. 3. Cambridge, near Central Square. 4. Topsfield, Mass. 5. Boxford, Mass. 6. New Haven, Conn., Yale University campus

[a] Micrograms of Se and mg. of S per liter of water or 100 cu. meters of air.
[b] Excluded from mean.

The Se/S ratio of various geochemical materials is summarized in Table II (Rankama and Sahama, 1950). In most cases the ratio Se/S $\sim 1 \times 10^{-4}$ is typical, but in sea water S is 1000 times greater relative to Se (Schutz and Turekian, 1965). If most of the atmospheric Se and S originated from terrestrial sources, including fuels and ores used in industry, a ratio of Se/S $\sim 1 \times 10^{-4}$ is expected, but if sea water is the source, a much lower relative abundance of Se is expected unless the sea-air transfer mechanism strongly enriches Se in the atmosphere. A question these preliminary analyses cannot answer is the relative atmospheric residence time of Se and S. If Se stays in the atmosphere for days or less, the average value of Se/S should decrease with increasing distance from the metropolitan area. On the other hand, if locally Se has a longer residence time than S, caused, for example, by peculiari-

ties of pollution sources, then Se/S could exceed the average value found in this work. Since Se is a toxic element as well as a useful indicator of the atmospheric chemistry of S, further investigation of Se in the atmosphere would be of value.

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Low Level Kjeldahl Nitrogen Determination on the Technicon AutoAnalyzer

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■ The existing procedures for the determination of Kjeldahl nitrogen on the AutoAnalyzer have been improved to provide greater sensitivity and reliability. Digestion temperatures of 400° C. provided improved stability. Sample flow rates of 2.5 ml. per minute and colorimeter flow rate of 3.6 ml. per minute, in combination with 0.01M Na nitroprusside as a color catalyst and 5-cm. colorimeter light path, provided a detection limit of 0.03 mg. per liter of nitrogen. Fifteen Kjeldahl analyses were performed per hour.

Difficulty was experienced in obtaining the sensitivity and stability required for the analysis of natural water samples using previously published procedures (Catanzaro, Goldgraben *et al.*, 1966; Ferrari, 1960; Ferrari, Catanzaro *et al.*, 1965) for the determination of low level total Kjeldahl nitrogen on the Technicon AutoAnalyzer. The following procedure is a modification of the previous procedures that enable the water analyst to perform large numbers of routine Kjeldahl nitrogen determinations with greater sensitivity and reliability.

The basic procedure involves digestion of the sample (natural water, in this case) with a sulfuric acid solution containing
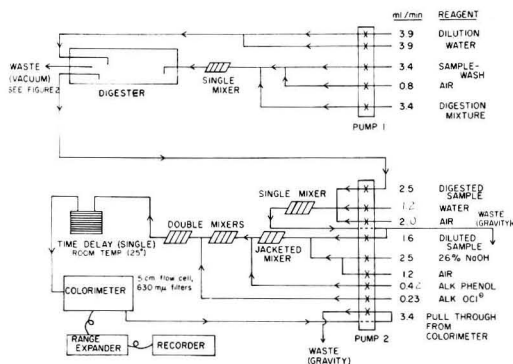
Figure 1. AutoAnalyzer flow diagram for low-Level Kjeldahl nitrogen

perchloric acid and selenium as a catalyst to convert amine- and amide-type organic nitrogen to ammonium. The digested sample is then made alkaline with a sodium hydroxide solution and treated with an alkaline phenol solution followed by an alkaline hypochlorite solution. This treatment results in the formation of an intense blue color described as an indophenol (Bolleter, Bushman, et al., 1961; Russell, 1944) that obeys Beer's law and is measured colorimetrically.

Experimental Procedure

Apparatus. The Technicon AutoAnalyzer system consists of: one sampler; two proportioning pumps with the manifolds shown in Figure 1; one colorimeter with 630-mμ filters, 5-cm. flow cell, range expander, and recorder; one continuous digester; one vacuum pump; two 5-gallon carboys; three 1-liter suction flasks for use as traps; and one single, unheated time delay coil.

Reagents. ACS grade chemicals were used unless otherwise noted.

DIGESTION SOLUTION (1 liter). Add 3.0 ml. of perchloric acid (60%) to 1 liter of 50% v./v. sulfuric acid solution, stir, then add 4.8 ml. of selenium oxychloride (technical grade, Baker Chemical Co.) to the solution and stir until the selenium oxychloride is completely dissolved.

SODIUM HYDROXIDE SOLUTION, 26% (about 1 liter). Dissolve 260 grams of NaOH pellets in 740 ml. of distilled water; cool the solution and transfer it to an alkaline-resistant bottle for storage.

ALKALINE PHENOL SOLUTION (1 liter). Place 250 grams of crystalline phenol in a 2-liter Erlenmeyer flask. Place the flask in a large vessel containing water and ice, or cool it with cold running water. Add 500 ml. of 20% NaOH solution to the flask slowly with constant mixing while keeping the flask cool. When the phenol is dissolved, transfer the contents of the Erlenmeyer to a 1-liter volumetric flask and dilute to volume with 20% NaOH solution. Store the solution in a polyethylene or amber glass bottle. Proper cooling and stirring during the slow addition of the NaOH will give a light-colored solution with a correspondingly low reagent blank.

ALKALINE HYPOCHLORITE SOLUTION (0.5 liter). Dissolve 35.7 grams of calcium hypochlorite (Matheson HTH, 70%) in 300 ml. of hot water (70° to 80° C.). Solution will probably be incomplete. Dissolve 40 grams of anhydrous K$_2$CO$_3$ in 200

ml. of distilled water; add 135 ml. of this solution to the calcium hypochlorite solution and stir. Heat the combined solution to 90° C. and cool rapidly. Dilute the solution to 500 ml. with distilled water. Filter a small portion of the solution and test for the presence of calcium ion as follows: To 1m l. of filtered solution, add 2 to 3 ml. of the K$_2$CO$_3$ solution prepared previously and heat the resulting mixture in a boiling water bath for a few minutes. If Ca is absent, the solution will remain clear. If the solution becomes cloudy, indicating the presence of Ca, add more K$_2$CO$_3$ solution to the hypochlorite solution and repeat the Ca test. When the test is negative, filter the entire solution and store it in an amber glass bottle. Commercial Clorox may be substituted for the alkaline hypochlorite solution.

AMMONIUM SULFATE STANDARD SOLUTION. Dilute 0.472 gram of ammonium sulfate to 1 liter with distilled water. The resulting solution is equivalent to 100 mg. per liter of ammonia nitrogen. Dilute this stock solution to give standards in the range needed.

The two pumping manifolds, shown in Figure 1, are constructed and arranged with the other basic AutoAnalyzer components as shown. The vacuum trap system used in conjunction with the digester is shown in Figure 2. The Auto-Analyzer instruction manual should be consulted for the details of putting the system in operation.

The following basic instrument settings were utilized:

Sampler	Digester
Sample time, 1 minute	Stage I, 4 amperes (350° C.)
Total cycle, 4 minutes	Stage II, 6.7 amperes (400° C.)

Range Expander	
10× for levels 0 to 5.0 mg. per liter of nitrogen	

Discussion

Most of the work that has been done on automated Kjeldahl nitrogen procedures has been directed toward clinical analyses (Ferrari, 1960; Ferrari, Catanzaro, et al., 1965) and industrial monitoring and quality control operations (Hofstader, 1956). These methods cover a concentration range of 50 to 5000 mg. per liter of nitrogen. Hofstader (1966) used the AutoAnalyzer to determine nitrogen in fertilizer and petroleum samples that had been digested manually. The ammonium ion formed was measured colorimetrically as the indophenol blue complex. Apparently, no range expansion was applied; standards ranged from 10 to 90 mg. per liter of nitrogen. For work with relatively unpolluted natural waters, 0.1 mg. per liter of nitrogen is a convenient maximum lower limit of detection.

Catanzaro et al. (1966) reported a procedure for low level nitrogen determinations that is a modification of an earlier procedure presented by Ferrari (1960). Increased sensitivity was attained by increasing the sample volume used, applying range expansion, and increasing the length of the colorimeter flow cell. Analyses were reported using this procedure for
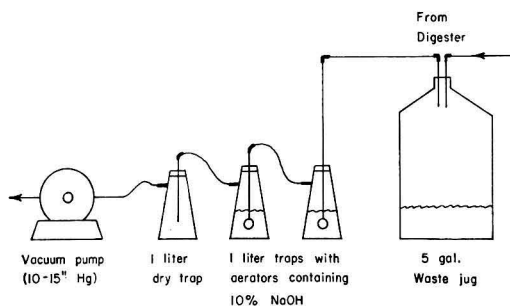
Figure 2. Vacuum trap system used with Kjeldahl digester

samples containing as little as 0.3 mg. per liter of ammonia nitrogen.

The procedure reported here is a modification of the Catanzaro procedure, which gives greater sensitivity and increased stability.

Sensitivity was increased by increasing the amount of digested sample withdrawn from the digester for analysis from 2.0 to 2.5 ml. per minute.

Stability was another problem. When the second stage of the digester was operated at temperatures above 400° C. for several hours, drying occurred in parts of the helix during rotation. This apparently caused sample material to be fused to the glass, causing a gradual decrease in sensitivity accompanied by a rising, noisy base line. A digestion temperature of 400° C. was adequate for complete digestion and recovery of organic standards tested (quinoline, urea, glycine) and did not affect the values obtained on previously analyzed water samples. The flow through the colorimeter cell was increased from 2.9 to 3.6 ml. per minute in an effort to prevent particulate matter from settling out in the flow cell.

The optimum pH for color formation is considered to be 11.4 to 11.6 (Mann, 1963). With the system at this pH, color formation is said to be enhanced by heating (Catanzaro, Goldgraben, *et al.*, 1966; Ferrari, 1960; Russell, 1944). This study showed that passing the sample stream containing the color-forming reagents through a heated 5-minute time delay coil decreased the intensity of the color formed. This decrease could be due to the length of the heating time or to the presence of excess sodium hydroxide. The presence of excess sodium hydroxide alone greatly decreases the sensitivity of the method.

The use of sodium nitroprusside as a catalyst for the color formation reaction has been reported (Mann, 1963). In the present work, a $0.01M$ solution of sodium nitroprusside was added to the system in place of the dilution water used to dilute the sample drawn from the digester. Roughly a fivefold increase in sensitivity was observed. The addition of more concentrated nitroprusside solutions (up to $0.03M$) increased the sensitivity slightly, but also raised the base line by 10% transmission. No effort was made to determine the optimum nitroprusside concentration since the sensitivity available, without the use of a color catalyst, was adequate for the samples encountered.

The lower limit of detectability, using the system described without a color catalyst, was 0.1 mg. per liter of nitrogen, using a range expansion of $10\times$. The estimated error for con-

centrations read on the $10\times$ scale is ± 0.1 mg. per liter for routine analysis. A range of 0.1 to 5.0 mg. per liter of nitrogen may be covered on the $10\times$ scale; for larger concentrations, the range expansion may be decreased.

The lower limit of detectability, using the system with a $0.01M$ sodium nitroprusside color catalyst, appears to be about 0.03 mg. per liter of nitrogen. The precision has not been estimated for values obtained using a nitroprusside color catalyst.

Recovery of Nicotinamide. Added quinoline, urea, and glycine were completely recovered with this procedure; nicotinamide was only partially recovered. Solutions of nicotinamide in distilled water were analyzed, and the following recoveries were noted:

Mg. per Liter of Nitrogen		
Calcd.	Found	Recovery, %
2.0	1.4	70
2.0	1.3	65
0.5	0.4	80

Interference of NO_2^- and NO_3^-. Although NO_2^- and NO_3^- should not be measured by the procedure used in this investigation, a check was made to be certain this was the case. Separate samples of untreated Lake Mendota water were dosed with concentrated solutions of sodium nitrite and sodium nitrate to give final concentrations of 5 mg. per liter of nitrite nitrogen, 10 mg. per liter of nitrite nitrogen, 5 mg. per liter of nitrate nitrogen, and 10 mg. per liter of nitrate nitrogen. These samples were analyzed along with a control that had been dosed with a volume of distilled water equal to the volume of nitrate or nitrite solution used (1 ml. per 100-ml. sample). The analyses for all samples were identical within the range of experimental error (± 0.1 mg. per liter of nitrogen) and equal to 0.6 mg. per liter of total Kjeldahl nitrogen.

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Water for Peace
The U.S. shifts gears

The 3500-plus delegates who gather in Washington in late May for
the International Conference on Water for Peace will find—not the offer of a massive
U.S. aid program—but rather a call for more local financing and local planning

...I want to announce the beginning of a Water for Peace Program.... Therefore, today I call upon all the nations of the world to join us in the creation of an international fund to bring the fruits of science and technology to all the corners of a parched and thirsty world. The United States is prepared to contribute its share of the resources needed for an international crash program to deal with world water resources.... [We] would convene within a year another great conference to deal with all the world's water problems....

<div align="right">

PRESIDENT LYNDON B. JOHNSON,
*October 7, 1965, before the
First International Symposium
on Water Desalination*

</div>

Now, 18 months after President Johnson's proposal, the International Conference on Water for Peace is in the final throes of planning. Specifics of the U.S. Water for Peace Program have been spelled out for the first time. A report by the Interdepartmental Committee on Water for Peace emphasizes that the proposed program is not an "international fund" or a "crash program," but that "through the Water for Peace Program the world community can exchange knowledge and experience, offer encouragement, supply technology, and provide technical and financial assistance, but one nation or region cannot do the job for any other. This principle of self-help is fundamental to the program."

The interdepartmental committee, established shortly after the President's proposal, is composed of representatives from many government groups interested in water programs. The chairman is Kenneth Holum, Assistant Secretary of the Interior for Water and Power Development. The committee recommended a U.S. Water for Peace Program and made these specific proposals:

• Provide more data and information about water problems, water resources, and opportunities for development.

• Provide more trained manpower to put knowledge and technology to work.

• Improve planning and organization of water programs at local, national, and regional levels throughout the world.

The committee also recommended that "many of these cooperative efforts be coordinated by, and channeled through, strengthened or newly established multilateral institutions at the regional and subregional levels."

Meeting plans

The upcoming meeting, according to Holum, "will not be an action conference. It is not a proper type of conference for taking action." Instead, the planners hope a much fuller picture of the world water picture will emerge. The meeting has three major objectives:

• Identify water problems.

• Explore ways of attacking them.

• Determine the international cooperation required to stimulate effective national and international water development programs.

Planning for the meeting has been hampered by lack of funds. Congress appropriated $500,000, instead of the $1.2 million requested to run the meeting, to be held in Washington, D.C., May 23–31. Still, meeting planners are pleased with the way the conference is shaping up. For example, registration is expected to be 3500–5000. To date, 85 nations, 12 international organizations,

and eight UN agencies have indicated they will participate.

Canada said it would participate in the conference only if the sponsors agreed that there would be no action taken—or even discussion—on any proposals to move Canadian water out of the dominion for use elsewhere. Of the Communist bloc countries, only Yugoslavia plans to participate. The U.S.S.R. was invited but declined to attend, possibly because East Germany and some other satellite countries were not invited.

Broad scope

Some 700 papers have already been submitted; they have been prepared by the U.S., 43 other nations, and 12 international organizations. About 200 will be presented orally at the conference at the expert level; the rest will be printed in the conference proceedings.

A wide range of subjects will be covered, including domestic and industrial water supply, irrigation and drainage, flood control, multipurpose project development, water quality control and water reuse, data collecting, weather modification, evaporation control, water shed management, water conservation, pollution abatement, and water desalting.

The conference program is being developed at two levels: one for various governments' cabinet-level ministers who are heading delegations, the other for experts and observers interested in specific phases of water resource development. The conference will consist of three plenary sessions, five daily concurrent sessions, a motion picture festival, and an exposition. So far, 12 governments, including the U.S., and 58 industrial organizations have reserved exhibit space in the exposition.

Visitors Flock to ACS Exhibit on ES&T

Mirror. Reflected in the exhibit's mirror that asks the question "Are you in the picture?" is Dr. Melvin J. Josephs, managing editor, ES&T

Message. When the button below the mirror is pressed, a photograph of an ACS committee in action appears and the observer is reminded, visually, that "Many ACS groups are working on pollution problems." At the same time, an audio message begins. Here, two visitors to the exhibit listen to the following statement: "Through its national committees, divisions, local sections, and publications, the American Chemical Society is studying man's environment, finding ways to manage it, defining problems, and reporting progress. Now under way is a comprehensive study of the science and technology of environmental improvement. The ACS Division of Water, Air, and Waste Chemistry holds symposia on topics related to pollution, and local section committees are dealing with the problem. The Society's newest publication, ENVIRONMENTAL SCIENCE AND TECHNOLOGY, brings together research, analyses, and critical reviews on all aspects of environmental management."

Good Earth. Alongside copies of ES&T's Author's Guide is a lighted photograph of a farmer plowing his fields. On the photo is the question, "Does the air you breathe where you work or live smell this fresh?" The visitor is then directed to sniff the freshly turned essence of earth emanating from an aperture in the taller stand to the rear

Exchange. Dr. James J. Morgan (left) chats with Dr. James P. Lodge, Jr., Chairman of the ACS Division of Water, Air, and Waste Chemistry, at a social hour held during the national meeting

153rd National
ACS Meeting
Miami Beach, Fla.
April 9-14, 1967
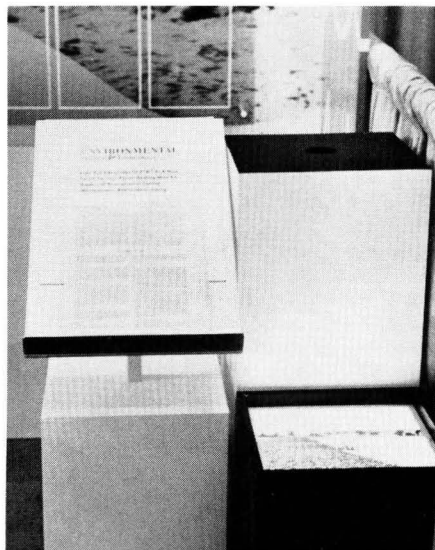
Cover. Standing in front of a stylized ES&T cover made of transparent blue plastic, Dr. James J. Morgan, editor, expresses pleasure with the full exhibit, which will be the core of a much larger ACS exhibit at the 31st Exposition of Chemical Industries (Chem Show) slated for New York City toward the end of the year

Fortuitous. Exchanging pleasantries about ES&T at a chance meeting brought about by the coincidence of a social hour for the University of Michigan and the Division of Water, Air, and Waste Chemistry are (left to right) Dr. James P. Lodge, Jr., Mrs. Charles C. Overberger, Dr. Charles C. Overberger (ACS President), Dr. James J. Morgan, and Dr. Melvin J. Josephs

NEW PRODUCTS DIGEST

Glass Circulating Pump

A compact unit for pumping acids, alkalies, buffer solutions, and organic solvents works with liquids from $-50°$ to $+100°$ C. The pump has a new type of spring-loaded seal which the company says ensures leak-proof joints, maximum corrosion, and wear resistance. Quickfit Reeve Angel, Inc. **61**

Bromide Ion Activity Electrode

Model 94–35 bromide ion activity electrode measures the activity of free bromide ion in aqueous and nonaqueous solutions. The electrode body is made from an unbreakable epoxy which is highly resistant to chemical attack. The electrode responds to bromide ion from saturated solutions down to 10^{-7} mole per liter, and is not affected by such common anions as fluoride, nitrate, sulfate, and phosphate ions. It can be used over the full pH range 0 to 14, at temperatures from $0°$ to $100°$ C. Also recently announced is an iodide ion activity electrode responding to iodide ion from saturated solutions to 5×10^{-8} mole per liter (ideal for analysis of water and industrial wastes and for biomedical research). Orion Research, Inc. **62**

High Precision Potentiometer

A direct-reading potentiometer designed for multipurpose laboratory use, the K-5 has a dual-angle case that holds the faceplate at about 30° for standing operators or 50° for seated operators. The range switch, decades, and slidewire are aligned from left to right in order of
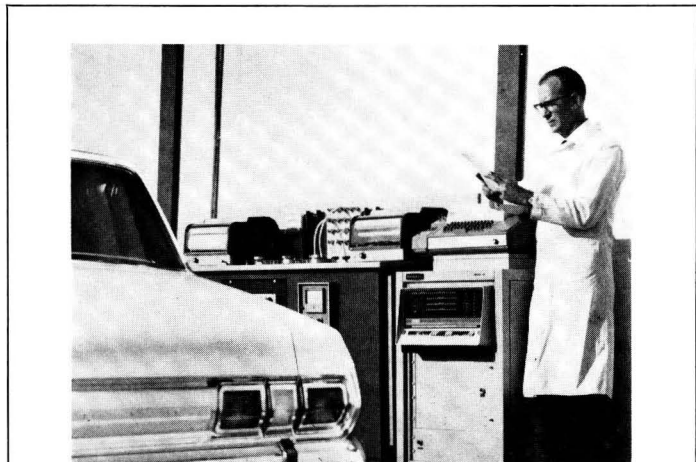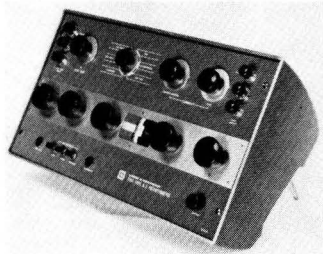
Vehicular Emissions Analysis

Specifically developed for simultaneous use with two Beckman/Scott Vehicular Exhaust Emissions Analysis Systems, the Model 82 data processor contains a small general purpose computer complete with an operating program to calculate exhaust emission test results. Two tests can be run simultaneously, even if they start and end at different times. The computer performs the calculations (which may take as long as two hours when performed manually) and stores results of the second test until the first test is completed; printout of stored data and test results from a complete test requires less than 10 minutes. Beckman Instruments, Inc. **66**

normal use. The limit of error on high range is $\pm 0.003\%$ of reading $+ 3$ $\mu v.$; resolution is 0.02 $\mu v.$ per division on low range. Leeds and Northrup Co. **63**

Flowmeters

A new line of low flow variable area flowmeters with interchangeable components is applicable to liquids, gases, or vapors within a maximum range of 0.5 to 2000 cc. of water or 38 to 59,000 standard cc. of air. The meters have heavywall glass tubes and fine control needle valves. Scale lengths available are $1^1/_2$, 3, and $6^3/_4$ inches. Fischer & Porter Co. **64**

Conductivity Measuring Bridge

The MC-1 is a portable battery-operated measuring bridge for determining the purity of water and the concentration of electrolytic solutions in laboratories and field applications. Supplied with two conductivity measuring cells of constants 0.1 and 100, the MC-1 covers conductivities of 0.1 to 100,000 micromhos/cm. in three ranges: 0.1 to 10 micromhos/cm., 10 to 1000 micromhos/cm., and 1000 to 100,000 micromhos/cm. The range of the instrument can be increased by connecting cells with constants other than those supplied. Chemicon Co. **65**

Digital Manometer

A new laboratory instrument for the measurement of very low pressure indicates pressure directly as a 4-digit reading rather than as column height. Overall accuracy, including linearity, is better than 0.5% measurement range. Three basic heads are available with nominal ranges of 0 to 10, 0 to 100, and 10 to 1000 mm. Hg. A sensitivity switch provides an additional measurement range of one tenth rated value for each head. The sensing head may be mounted at a remote measuring point (using an extension cable provided for interconnection). Whittaker Corp.   **67**

Measuring Completeness of Reaction

Model 691R ORP-to-current converter is available for use where measurement of the degree of completion of a chemical reaction is important. The all-solid-state converter can operate in a panel or in the field with a NEMA III (weatherproof) casing. The instrument has an input resistance of 0.5×10^{12} ohms, and measures from -2200 millivolts to $+2200$ millivolts. The M/691R can be located 1000 feet or more from the measuring electrodes without degradation of response characteristics. The instrument can operate from $-20°$ to $+140°$ F. Foxboro Co.   **68**

Teflon Joint Sealant

A new joint sealing compound uses Teflon in a thixotropic paste to seal threaded joints. Noncontaminating and

physiologically inert, the sealant has a service temperature range of $-400°$ to $+500°$ F. One tube of the compound, Formula 8, contains sufficient paste to seal 100 1-inch pipe joints. Fluoramics, Inc.   **69**

All Scott Research gas mixtures have a guaranteed analysis...

in other words our gases are standard gases

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

Write for our new specialty gas catalog E.

SCOTT RESEARCH LABORATORIES, Inc.

Dry PVC Fan/Scrubber

The successful conclusion of a six-month, in-service field test for exhausting concentrated sulfuric acid fumes with a polyvinyl chloride fan/scrubber running dry was announced recently by Tri-Mer Corp. The installation which was tested consisted of two fan/scrubbers each exhausting 6000 c.f.m. from a plat-

ing plant copper recovery system. The units had been operating as originally designed with water spray introduced into the fan chamber. For the test, however, use of water was eliminated, allowing the return of undiluted sulfuric acid condensate directly to the copper-electroplate process tank, rather than being handled as waste. The dry operation produced no trace-sulfuric at the stack discharge, eliminating an air-pollution potential. Tri-Mer Corp. **70**
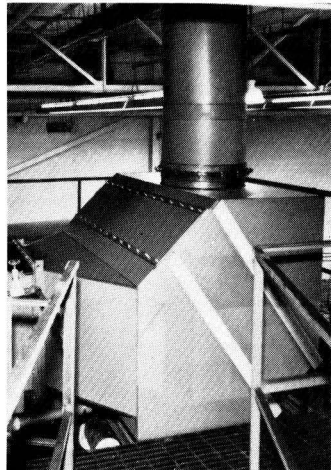
High Voltage Power Supply

A high voltage power supply delivers 500 to 1000 volts, continuously adjustable. The current limit on the silicon solid-state unit can be set from 0.5 to 3.0 milliamperes to protect the photomultipliers or other high voltage equipment being used. McKee-Pedersen Instruments. **71**

Silicone Adhesive sealant

Silastic 737 RTV adhesive sealant maintains rubbery consistency from −85° to +350° F. and will tolerate short or intermittent exposures at temperatures as high as 500° F. The sealant withstands contacts with hot oils, free steam, immer-

sion in water, prolonged hot and humid conditions, oxygen, ozone, and ultraviolet rays. Durometer hardness on the Shore A scale is 35 and tear strength is 100 p.s.i. Available in 2-oz. collapsible tubes and 12-oz. cartridges. Dow Corning Corp. **72**

Reverse Osmosis System Components

Membrane cartridge modules, pressure containers for modules, and flow control devices are now available in three sizes (for 2.5, 5, and 20 square feet of active membrane area) from stock supply. The membrane cartridge modules, which use the Desal model MF-10 membrane, reduce salt content of brackish water 80 to 90% with a feed water pressure of 100 p.s.i. and will remove all particulate material and almost all large molecules dissolved in the feed water. Desalination Systems, Inc. **73**

Ultraviolet Filter Photometer

For applications requiring continuous monitoring of nitrogen dioxide, the Model 255 ultraviolet filter photometer can also be used in the analysis of many other compounds which absorb light in the 400 mμ. wavelength region. Results are obtainable in seconds, whether in the p.p.m. range or 100% concentration. Simplified optics, controls, and electronics permit convenient operation. The unit has a repeatability of ±1% of full scale, and operates from 40° to 104° F. Beckman Instruments, Inc. **74**

Infrared Thermometer

An all-purpose fixed-unit radiation pyrometer for precise and continuous temperature measurement, monitoring, and control operates without contacting the system being measured. Infrared radiation from a precisely defined area is focused by the optics in the instrument onto a sensitive infrared detector which converts the received radiation to an electric signal. This electric signal is amplified to provide a 0 to 10 mv. output to recorders, controllers, or indicators. Continuous process control is thus made available for materials which are in motion, fragile, or are in inaccessible areas. Various temperature ranges from 100° to 3000° F. are available. Accuracy is ±1% and sensitivity is 0.25% of full scale. Thermo Electric Co., Inc.   **75**

Laminar Flow Burner

A new nitrousoxide-acetylene flow burner is capable of obtaining flame temperatures to 3000° C. and uses an integral heating-condensing device that minimizes the amount of solvent reaching the flame and, thus, helps maintain sample purity. The unit is equipped with an automatic heater switch to prevent overheating and an automatic fuel shut-off in case of low support gas pressure. Beckman Instruments, Inc.   **76**

Activated Charcoal Air Filter

A sectional type device uses high grade activated coconut-shell charcoal to remove odors and other gaseous and vaporous contaminants from an air stream. Called the FJD Adsorber, the cubical device (24 inches on a side) has a velocity of 2000 c.f.m., a pressure drop of 0.3 inch water gage, and removes 95% of the contaminants on a single pass. The adsorber is usually used in conjunction with high-efficiency particulate filters (placed upstream of the adsorber to protect the charcoal). Barnebey-Cheney Co.   **77**

Vacuum Oven

A multipurpose drying apparatus for work with reduced pressures and inert atmospheres, the Model 48 vacuum oven provides generous capacity (313 sq. in.), precision temperature control (accurate to 1.0° C., average temperature deviation ±1.5° C. at 100° C. and ±3.5° C. at 200° C.), and stainless steel construction to resist corrosion and contamination. The unit holds vacuums from 1 atm. to 30 inches of mercury and controls temperatures from 30° to 200° C. Fischer Scientific Co.   **78**

Analytical Balance

An analytical balance especially designed for fast, accurate air pollution analysis weighings utilizes solid-state electronic null indication and friction-free torsion mechanism. The electronic null indication system provides 7 times more weight deflection per 0.1 mg. of weight change than many optical systems; readability is 0.05 mg. Capacity of unit is 160 grams and precision (standard deviation) is ±0.03 mg. Torsion Balance Co.   **79**

The Soil
As a Living Filter

A group of Pennsylvania State University scientists have made a photographic record of a series of experiments designed to determine the efficiency of soil as a living filter for waste waters. The four-year experiment in converting land to a living filter demonstrated that only 1290 acres of crop land are needed to dispose of the waste water from a city with a population of 100,000.

A 16-mm. black and white motion picture (with sound track) explains the test process and the ecological effects. The film shows the piping system used to spray waste water over crop and forest land (left, winter operation; right, summer operation); the sampling and monitoring techniques employed by the university, and the wildlife studies carried on simultaneously with the experiment to determine whether the program has deleterious effects on local fauna.

Nitrogen and phosphorus compounds, which are difficult to remove cheaply from water, are readily captured by the soil. Phosphorus concentrations, for example, were reduced 99% at the 4-foot test depth. Nitrogen and phosphorus compounds, when dumped in streams, upset the balance of nature and cause all sorts of problems involving fish and other aquatic life while speeding the natural aging process through which all lakes and streams grow.

Besides showing how the soil may be used in the efficient removal of nitrogen and phosphorus from the treated sewage effluent, the program has resulted in recharging underground reservoirs and sharply increased crop production. Also, crops grown on the test plots have a higher mineral content than control crops. If the plots are to be used regularly for water filtration, the crops must be harvested to prevent redeposit of the nitrogen and phosphorus in the soil.

The film may be borrowed, free of charge, from the Department of Public Information, Pennsylvania State University. Please circle **80** on the Readers' Service Card.
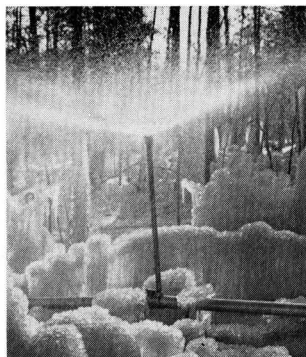
Submersible pumps. A handsome, full color, 12-page brochure features a capsule history of Flygt electric submersible drainage pumps for construction, sewage, and mining applications. Titled "The Heart—Nature's Pump; the Pump—a Mechanical Heart," the brochure includes color photographs of the company's currently available models. Flygt Corp. **81**

Line-operated pH meters. A 6-page illustrated folder describes four line-operated pH meters, including a new expanded-scale meter. The folder contains descriptions, specifications, prices, and photographs of each of the four meters, and a comparison of performances. Leeds & Northrup Co. **82**

Infrared spectrophotometer accessories. Liquid sampling accessories for infrared spectrophotometers are the subject of a 4-page bulletin. Developed by Research and Industrial Instruments Co., Beckman's London subsidiary, the accessories include three types of variable path length cells, fixed path length cells, throwaway cells, and sealed and demountable cells. Beckman Instruments, Inc. **83**

Valve catalog. A 4-page catalog contains illustrations, line drawings, and dimensional charts for standard, manifold, and column mount values. The quick acting, packless, and permanently tight valves are available in six sizes, ranging from $1/4$- to $1 1/4$-inch. Rex Chainbelt, Inc. **84**

Wet vacuum pumps. A 12-page bulletin describes the features, operating principles, and advantages of a redesigned wet vacuum pump. Available in capacities ranging from 1000 to 23,000 c.f.m., the pump was designed for the paper industry for use with wet vacuum filters and features a new, high displacement, water-sealed impeller profile. The bulletin contains photographs and drawings of the wet vacuum pumps, showing how they operate in actual plant applications. Fuller Co. **85**

Laboratory equipment. Approximately 30 new products are described in this 16-page supplement to the 1966 products catalog. Operating specifications, photographs, and prices are included for each item. Scientific Glass Apparatus Co., Inc.   **86**

Gas and gas usage equipment. A catalog of compressed gases, equipment, and gas mixtures lists more than 110 compressed gases for laboratory use, including such gases as ozone, germane, and arsine. A large section on gas usage equipment includes specially designed regulators, flowmeters, valves, gas detectors, a cryogenic liquefier, and gas handling equipment. A 12-page gas mixtures section includes both weight standard mixtures and p.p.m. mixtures. Matheson Co., Inc.   **87**

Honeycomb catalytic stack purifier. A fact sheet on Oxy-Comb Catalytic Honeycomb Units for the removal of smoke odors and harmful elements from industrial stack gases is available. A special patented process produces a very high specific surface area in the unit, resulting in small space requirements and low initial cost for installation. Oxy-Catalyst, Inc.   **88**

Condensate purification units. A 15-page report, "Factors in Selection of Condensate Purification Equipment for Once-through Boilers," discusses the place of the condensate purification unit in the power system, the chemical considerations necessary in the design of the preboiler cycle, including condensate purification and the problem of condenser leakage. The report also discusses initial and operating costs of the various methods of condensate purification. Graver Water Purification Co. **89**

Dust collectors. Information on a series of large-tube dust collectors is given in a 6-page bulletin. The collectors are for clinker cooling and kiln exhausts, sintering and pelletizing furnace outlets, coke and coal dust collection, and other applications where dust concentration is high, the dusts are highly abrasive, or collection problems are critical. The standardized unit and optional features available are described. The bulletin features a collector efficiency monogram to aid in selecting the collector needed for a specific application. American-Standard, Industrial Division.   **90**

Radioactive waste solidification. Use of platinum melters for radioactive waste solidification is discussed in the *Engelhard Industries Technical Bulletin*. The December 1966 issue also includes a paper on a new family of catalysts for nitric acid tail gases. Engelhard Industries, Inc.   **91**

Selenium. A 6-page bulletin summarizes briefly the technical papers of the first International Symposium on Selenium in Biomedicine. Selenium-Tellurium Development Association, Inc.   **92**

New journal. First issue of the new quarterly publication, *Pesticides Monitoring Journal*, scheduled for June, will detail the national pesticide monitoring programs of various federal and nonfederal agencies. Federal Committee on Pest Control.   **93**

BOOKSHELF

Pesticides: An Approach to Integrated Control

Scientific Aspects of Pest Control. A symposium. xi + 470 pages. Publication 1402, National Academy of Sciences–National Research Council, Washington, D.C. 20418. 1966. $5.00 paper. *Thomas J. Sheets is Project Leader, Pesticide Residue Research Laboratory, North Carolina State University at Raleigh, Department of Entomology, School of Agriculture and Life Sciences.*

By Thomas J. Sheets

Uses of pesticides in agriculture, public health, and forestry have been the objects of much criticism and condemnation by some segments of our society. Others herald organic pesticides as a major twentieth-century technological development that permits man, in his ever-increasing numbers, to avoid mass starvation through greatly increased food production. *Scientific Aspects of Pest Control* is the published form of a symposium which was arranged and conducted by the National Academy of Sciences–National Research Council, to present publicly the "status of our knowledge on pest control, the degree to which control programs are achieving their objectives, and the problems that need further attention."

Details on methods of controlling specific insects, weeds, plant pathogens, or other pests are not cataloged in this book. More appropriately, the authors delve into the philosophies of pest control, pesticide use, other methods of pest control, benefits and harms from pesticide use, fate and effects of pesticides in the environment, and public policy and regulations.

Most of the authors present unbiased views and recognize the essentiality of pesticides to agriculture and to public health. The writings are easily readable and are infused with interesting, noteworthy, and sometimes striking examples, all of which maintain reader interest. Subject matter is well organized and logically presented. The authors are leaders of renown in their fields; they have presented sound factual information and, in most instances, thoroughly covered the assigned task.

Integrated control

However, a few comments on completeness of coverage and philosophies are in order. Integrated control is a general theme of a few chapters. This is a valid, scientifically sound, and highly desirable approach to pest control. The chapter which bears the title "Integrated Control Systems" is a well-organized and thorough discussion of the topic in relation to insect control. Although not known by that specific name, integrated control has been practiced purposely for many years, especially in weed and plant pathogen control. The author recognizes this but indicates that integrated control has not been organized "to bring together and harmonize several suitable techniques." This system has, in fact, been employed in systematized fashion for many years, especially in weed and plant pathogen control, but perhaps to a somewhat more limited extent in insect control. Need for additional research to evaluate and extend the use of integrated control systems is clearly and effectively presented.

One chapter deals specifically with insects, one with weeds, one with plant pathogens, and one with vertebrate pests. In other chapters, however, insects and insecticides receive, by far, the greatest attention and are employed, in most instances, as examples of problems or principles. Although some readers may be inclined to regard this trend as biased, insecticide residues have caused by far the most severe and greatest number of environmental contamination and human safety problems.

Biological control is considered extensively in several chapters and justifiably so; its successes are discussed, often in considerable detail. Possibilities for failures and shortcomings of biological control methods are stressed in the chapter dealing with plant diseases and are clearly pointed out in the chapter on weed control. On the other hand, possibilities for resistance of insects to biological control agents, a point often made as an argument against the use of pesticides, was not considered in its relative importance in several chapters— although it was mentioned in passing.

The chapter on metabolism and fate of pesticides in plants and animals is a refined and complete discussion. Similar comprehensive treatment of persistence and degradation of pesticides in the environment would have been desirable. Although frequently discussed in relation to specific topics throughout the book, persistence of pesticides in the environment and associated problems are not treated in a single chapter as comprehensively as our knowledge permits.

Several obviously conflicting opinions are presented by several authors, but these different views appropriately provide the ideas and information to meet the broad objectives of the symposium. Conflicting views are presented with sincerity and humility, generally, with appreciation and respect for others' points of view. From the diversity of backgrounds, professions, and interests of the authors, one would expect disagreement on pesticide use; and some disagreement is highly desirable on a subject with so many benefits, but with hazards and occasional problems, sometimes of an insidious nature.

Restatement and projection

In the final chapter many ideas discussed throughout the book are brought together, problems are restated and discussed, and research needs and prospects for the future of the entire field of pest control are summarized. Ideas, problems, and research needs are ef-

fectively placed in proper perspective there.

Research workers in pest control and in related fields such as toxicology and ecology should read the book and study the ideas presented. The contents are so diverse (yet related to pest control) that few research workers, if any, are familiar with all of the topics covered; and many problems, problem solutions, and ideas, although not in all cases new, are not generally known or are presented from a different point of view and with different emphasis. The book is of special value to scientists of other fields and is of interest even to the rather casual reader who wants to become familiar with broad aspects of pest control.

In spite of a few possible omissions and shortcomings, perhaps of a minor nature depending on one's point of view, the book is an excellent contribution to the scientific literature. This volume is the most comprehensive treatment available on the general aspects and philosophies of pest control.

Man's Careless Pesticide Use Can Defile Environment

Organic Pesticides in the Environment. Edited by Robert F. Gould. x + 309 pages. American Chemical Society Publications. Washington, D.C. 20036. 1966. $8.50 hard cover. *Louis Lykken is Associate Specialist, Division of Entomology, University of California, Berkeley, Calif.*

By Louis Lykken

Our environment—the air, water, and soil around us—is the final repository of all products produced by the inhabitants of this planet and by the physical and chemical processes taking place on it. The kind and extent of the defilement of our environment is of inevitable concern to all mankind, be they laymen, scientists, or engineers. There is good cause for concern because of the possible effects that contaminants may have on the ever-increasing human population, useful animals, and plants.

Pesticides hold a unique position among contaminants because they are directly applied to our environment and have a deadly effect on the target organ-

isms. It is this concern and position that evoked the technical symposium from which the papers for the volume under review were drawn. Likewise, this concern generated a number of legislative committee reports dealing with the pollution problem.

Organic Pesticides in the Environment comprises 23 of the 29 papers that were presented at the aforementioned symposium. The papers are essentially independent articles, many of which deal with narrow facets or aspects of the general subject. By and large, the papers are well written and free from factual errors, and all are worthy of publication even though some of them have, at best, only a tenuous interrelationship, and several do not pertain to the subject of the book. Thus, the book is essentially a vehicle for publication of the symposium papers and, obviously, it is not the result of an attempt to develop the subject in a systematic manner. Therefore, while the specific articles have important reference value, the book is not a comprehensive reference volume on the subject and does not present a well-rounded picture.

The first paper describes the types of pesticide chemicals currently in use and briefly gives the important chemical, physical, and toxicological properties of important compounds in each type. The third paper, which is very much to the point, deals with the biological effects of pesticides in the environment from the standpoint of threshold dose levels, levels of occurrence, and the like; it points out the great need for more data in this area and the need for good monitoring organization to assess the degree of contamination in various geographic areas.

Most pertinent

The ninth and nineteenth papers are the most pertinent ones. The former deals with the occurrence, sources, and mode of introduction of pesticide chemicals into the environment and with the transport of pesticide chemical residues, and paints a broad picture of the problem. The latter discusses interrelated factors pertaining to the fate and persistence of these chemicals in the environment, especially degradation in or on plants and metabolism in animals, and (in some duplication of paper nine) discusses the occurrence and persistence

of their residues in soil, water, and air.

Several papers deal wth contamination of the environment with pesticide chemicals in a rather specific, restricted way. One paper considers exposure of dairy animals through respiration, another deals with residue distribution in a treated plot, and a third considers levels of residues of three chemicals in certain waterways. Another deals with translocation of residues by air transport and rain-out but emphasizes analytical methodology. A fifth concerns itself with the details of sampling and analysis of herbicidal chemicals in connection with a restricted survey of atmospheric contamination. And a sixth deals with the persistence of certain residues in orchards. Another paper discusses the persistence of a specific herbicide in aquatic environments. Almost all of these emphasize the analytical aspects of the subject.

The final paper in the book deals with physical and thermodynamic parameters involved in the removal of a variety of pesticide chemicals from water by sorption, but does not show reduction to practice. The second article concerns the sorption and leaching of a specific herbicide in soils, dealing primarily with factors involved and the nature of the sorption. Another deals with the need to predict pesticide levels in soils and the mathematics involved.

Wide variety

Four of the papers go into the potential and actual toxicological hazard from exposure to pesticide chemicals in the environment, and related aspects, generally being involved with specific chemicals and conditions. Three deal with the analysis and identification of pesticide chemicals in water, mud, or tissue of fish. And one concerns the metabolism of herbicides in soils, emphasizing pathways and enzyme systems. The wide variety of subjects is evident as is the vague tie-in that some of them have to the subject of the book.

The book is important as a medium for publishing most of the papers given at the symposium. The main positive feature of the book is that it contains several outstanding articles about the source, occurrence, persistence, biological effect, and fate of pesticide chemicals in the environment. On the other hand, I think it is a pity that the paper on countermeasures and control

of pesticide chemicals in the environment was not included in the collection. The main negative feature of the book is its lack of continuity and logical development of the subject, and its inclusion of some extraneous papers. However, despite these shortcomings, the book, all in all, is a worthwhile contribution to the literature.

Theoretical and Experimental Biophysics. Edited by Arthur Cole. xi + 397 pages. Marcel Dekker, Inc., New York, N.Y. 10016. 1967. $17.50, hard cover.

Rapid Survey Technique for Estimating Community Air Pollution Emissions. Guntis Ozolins and Raymond Smith. vii + 77 pages. Public Health Service, Division of Air Pollution, Cincinnati, Ohio 45226. 1966. No charge, paper.

Atmospheric Emissions from Nitric Acid Manufacturing Processes. PHS Publication No. 999-AP-27. vii + 89 pages. U.S. Government Printing Office, Washington, D.C., 20402. 1966. 40 cents, paper.

The Middle Ultraviolet: Its Science and Technology. Edited by Alex E. S. Green. xii + 390 pages. John Wiley & Sons, Inc., New York, N.Y. 10016. 1966. $15.75, hard cover.

Mechanistic Organic Photochemistry. D. C. Neckers. xii + 320 pages. Reinhold Publishing Corp., New York, N.Y. 10022. 1967. $14.75, hard cover.

Thorium: Its Industrial Hygiene Aspects. R. E. Albert. xii + 222 pages. Academic Press, Inc., New York, N.Y. 10003. 1966. $7.00, hard cover.

Pesticides and Their Effects on Soils and Water. ASA Special Publication, Number 8. viii + 150 pages. Soil Science Society of America, Inc., Madison, Wis. 53711. 1966. $2.00, paper.

The Pesticide Problem: An Economic Approach to Public Policy. J. C. Headley and J. N. Lewis. xvii + 141 pages. The Johns Hopkins Press, Baltimore, Md. 21218. 1967. $3.50, paper.

Water Production Using Nuclear Energy. Edited by R. G. Post and R. L. Seale. ix + 396 pages. University of Arizona Press, College Station, Tucson, Ariz. 85700. 1966. $7.50, hard cover.

MEETING GUIDE

May 1–5
American Industrial Hygiene Association, American Conference of Governmental Hygienists
American Industrial Hygiene Conference—1967
Pick-Congress Hotel, Chicago, Ill.

In addition to a wide-ranging program on matters pertaining specifically to health, the conference plans sessions on air pollution, atmospheric diffusion, sulfur dioxide, abatement, noise effects and controls, radiation hazards and controls, stack design, and building re-entry of fumes.

May 2–5
New York Academy of Sciences
Biological Effects of Pesticides
Waldorf-Astoria Hotel, New York, N.Y.

The conference is directed especially to members of the scientific community who are in a position to contribute to the further sophistication of research on health and related aspects of pesticides. Conference participants will include world authorities on toxicology, metabolism, mode of action, and epidemiological effects of pesticides.

May 15–17
American Petroleum Institute's Division of Refining
32nd Midyear Meeting
Statler Hilton Hotel, Los Angeles, Calif.

In sessions directed to research chemists, air and water pollution consultants, petroleum refiners, and others, API plans discussions on such subjects as reducing automotive emissions, reducing sulfur content of fuels, solving corrosion problems, and the effects of lead on health.

May 15–17
U.S. Atomic Energy Commission, Ecological Society of America, University of Michigan
Second National Symposium on Radioecology
Horace H. Rackham Lecture Hall, University of Michigan, Ann Arbor, Mich.

Subtitled Nuclear Energy in Man's Environment: Past, Present, and Future Problems, the symposium is designed to acquaint ecologists with the problems arising from the release of radiation to the environment—and how such problems have been treated in the past, so that future radiation hazards may be dealt with adequately.

May 15–18
American Association for Contamination Control
Sixth Annual Technical Meeting and Exhibit
Sheraton-Park Hotel, Washington, D.C.

Contamination control problems and solutions that are typical of hospital operating rooms, pharmaceutical and biological laboratories, and industrial and aerospace clean rooms will be discussed.

May 23–31
U.S. Departments of State and HEW
International Conference on Water for Peace
Sheraton-Park Hotel, Washington, D.C.

The conference has been developed at two levels: one for cabinet-level ministers who will head delegations, the other for experts and observers interested in specific phases of water resource development. For further details, see the discussion on page 345.

June 1–2
Vanderbilt University School of Engineering
Sanitary and Water Resources Engineering Conference
Noel Hotel, Nashville, Tenn.

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

June 4–9
American Water Works Association
87th Annual Conference
Atlantic City, N.J.

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

June 11–16
Air Pollution Control Association
60th Annual Meeting
Sheraton-Cleveland Hotel, Cleveland, Ohio

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

June 11–16
National Research Council (Division of Biology and Agriculture)
International Symposium on Eutrophication
University of Wisconsin, Madison, Wis.

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

June 12–16; 26–30
Manhattan College, Federal Water Pollution Control Administration
Twelfth Summer Institute in Water Pollution Control
Manhattan College, New York (Bronx), N.Y.

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

June 15–16
U.S. Departments of Agriculture and Housing and Urban Development
Soil, Water, and Suburbia
Jefferson Auditorium, Department of Agriculture, Washington, D.C.

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

MEETING GUIDE continued

June 21–30
University of California, Berkeley

Combustion-Generated Air Pollution
Berkeley, Calif.

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

July 3–7
Gordon Research Conference on Environmental Sciences

Air Pollution: The Oxides of Nitrogen
Crystal Inn, Crystal Mountain, Wash.

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

July 5–8
National Society of Professional Engineers

33rd Annual Meeting
Statler-Hilton Hotel, Hartford, Conn.

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

January 22–26, 1968 (Tentative)
Instrument Society of America

Fourth Marine Sciences Instrumentation Symposium
Melbourne, Fla. (Tentative)

The theme of the symposium will be directed to the problems of marine instrumentation, especially data recording, handling, and processing. Those who wish to participate in the symposium are invited to send a letter of intent to submit a paper (including title and abstract) to: Mr. H. W. Dubach, National Oceanographic Data Center, Washington, D.C. 20390

June 23–28, 1968
American Society of Testing and Materials

Materials and Their Performance in the Marine Environment
San Francisco, Calif.

Sessions are planned on the performance of materials in deep sea and coastal waters and at environmental interfaces; structures in the sea and the stress and fatigue which they undergo; new materials in sea applications; and high pressure environmental testing facilities. Those wishing to contribute papers should submit titles and abstracts no later than Sept. 1, 1967, to: Mr. H. W. Dubach, National Oceanographic Data Center, Washington, D.C. 20390.

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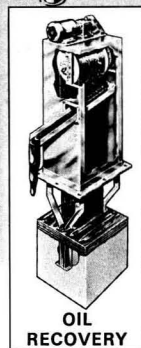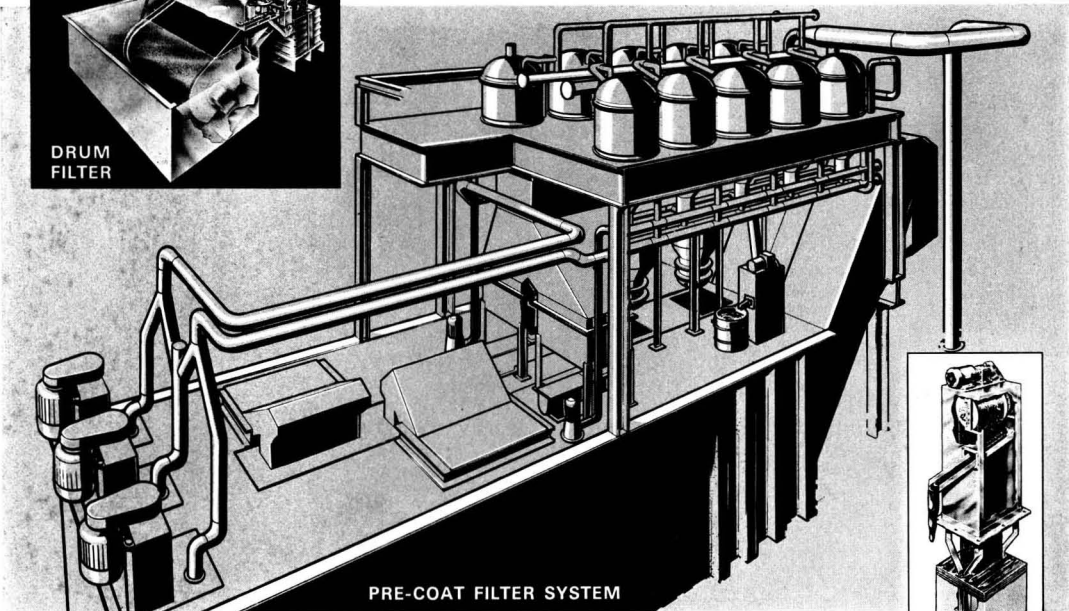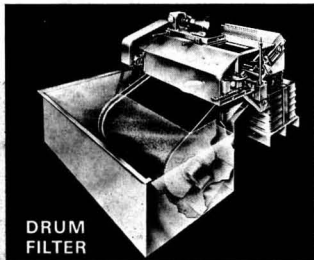
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