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Chemistry

JANUARY 1968
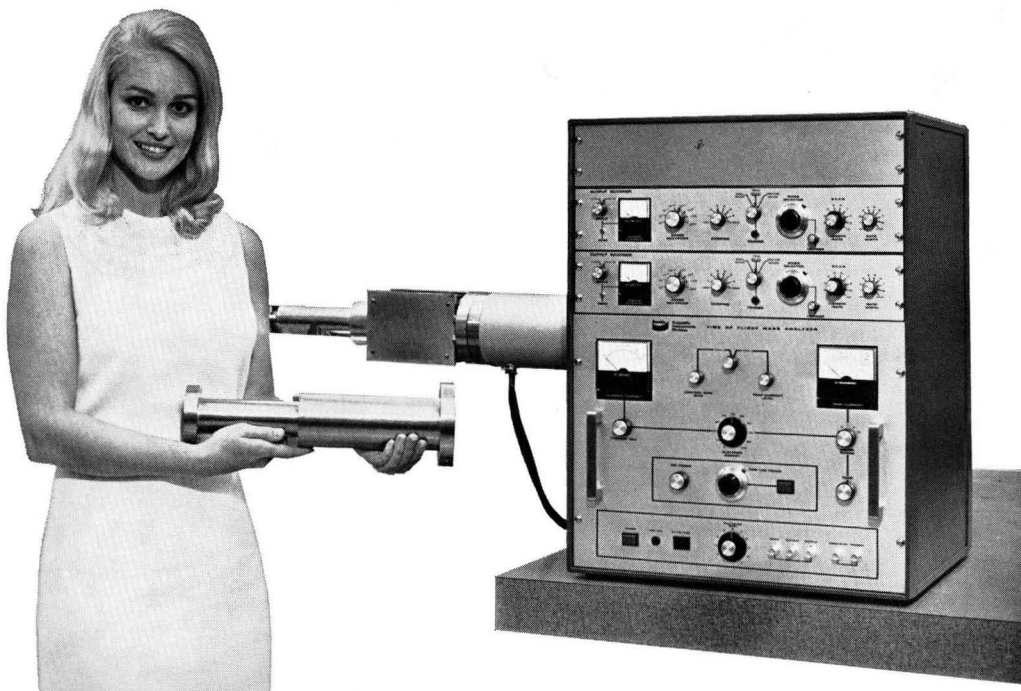
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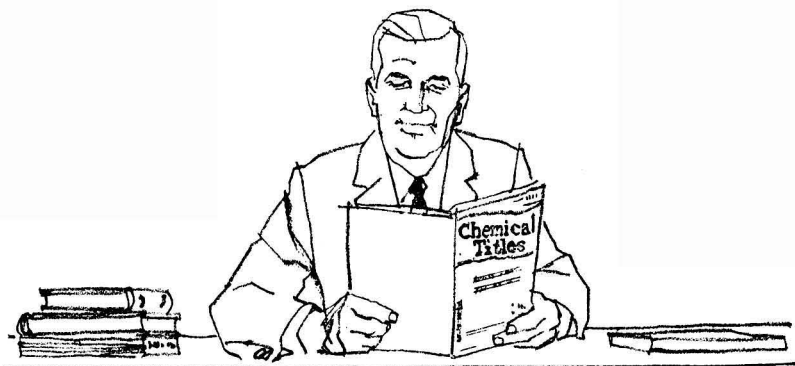
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Two ways to find out what's being published in the world of chemistry...

ENVIRONMENTAL
Science & Technology

CONTENTS

People can engineer for human fulfillment

If a single program to provide maximum economic, health, and social benefits had to be chosen for an underdeveloped region, that program would nearly always be to develop reliable water supplies

In our sophisticated, affluent society we are more often troubled by problems of too much and too soon than of too little and too late. Fortunately, our too much and too soon are relatively easy to live with. But much of the rest of the world's too little and too late are not easily ignored, and should not be easily tolerated.

Take, for example, the problems of water supply in Latin America (see page 17). Whereas we in the United States are now very much concerned—and rightly so—with setting water quality standards, huge areas and large populations in Latin America are concerned solely with the task of obtaining some potable water.

Picture the extent and magnitude of the job to be done there. According to the World Health Organization, as recently as 1961 almost no city in Latin America had water under pressure all day, every day of the week. Or consider the tribulations of living in a town of 25,000 where water is available only in the town's center, and there from only three small pipes which deliver water, under very low pressure, for only three hours on only three mornings of each week.

Happily, new and exciting solutions and techniques to overcome these difficulties are available, or are in the process of being developed. Indeed, considerable progress has been made toward supplying potable water to Latin Americans—66% of the urban population and 19% of the rural population are by now served by house connection or public hydrant.

Yet a formidable task remains. Sewage facilities are seriously deficient—only 53% of Latin America's people live in houses connected to a sewage system. But in this instance, too, the Latin Americans are making progress. Learning from the difficulties of the two-organization water supply–sewage disposal system that evolved in the U.S. in the 1930's and has persisted since then, Latin Americans are taking a combined approach—water in and sewage out as a package program.

Once Latin Americans have achieved the minimal goals of an adequate water supply and an effective sewage disposal system they will be able to turn their attention, as others have started to do, to the task of letting man look on the positive side of health. It is in this added, special way that the exercises of the environment manipulators can bear their most joyous fruit. It is the reduction to practice, the translation of the philosophical into the pragmatic, that leads to the betterment of man.

Health is not just the absence of disease and disability, says Surgeon General, William H. Stewart (see page 21). The healthy man is more than "unsick"; he is strong. The truly healthful environment is not merely safe but stimulating; it is a goal for all seasons and for all men.

Melvin J. Josephs

Eutrophication Task Force Seeks Standardized Procedure

Algal blooms on lakes can be a sign of accelerated eutrophication, but scientists have not always agreed on a best or standard technique for measuring the capacity of a lake to grow algae or the tendency of chemicals to stimulate alkal growth. The Joint Task Force on Eutrophication, composed of Interior Department and detergent industry representatives, is now going to try to develop a standardized procedure to determine algal growth potential (AGP). The Soap and Detergent Association, meanwhile, is pursuing other approaches to the possible role of phosphates (largely from detergents) in eutrophication. One is to seek substitutes to phosphates, an effort Interior recently applauded. However, the association cautions, extensive research has not so far uncovered a suitable substitute. Thus, the association believes, removal or control of nutrients is "of primary importance in the overall effort to control eutrophication."

Industry and Government Fight a Losing Air Pollution Battle

It calls itself the "Big Sky" country. Actually, it's the "Dirty Sky" country. And Montana is likely to remain so for some time, says C. C. Gordon, University of Montana botany professor. He attributes this situation to the apathy of government (at all levels) and the obstruction of industry. The governor vetoed a potentially effective air pollution bill in 1965; a bill was finally enacted in 1967. Industry then tried strenuously—but unsuccessfully—to persuade the State Board of Health to set nonstringent standards for ambient air. State agencies continue to refuse to talk of pollution—unless it is politically or economically advantageous. Typical of the problems is the fluoride pollution in Garrison (ES&T, September 1967, page 686). Since 1963, the emissions from a small phosphate plant have crippled cattle and killed vegetation within an eight-mile radius. Only after long inaction by state and local officials did the Federal Government act. But the Federal Government has not acted in Columbia Falls, where hydrogen fluoride from the Anaconda Co.'s aluminum plant is causing severe damage to conifers on Forest Service land. Another example of the problems, Gordon told the New York meeting of the American Association for the Advancement of Science, is the way Anaconda, "the state's largest single taxpayer and major polluter," continues illegally to dump copper mine wastes in the Clark Fork of the Columbia River.

Council Checks for Foul Flavor Fish Flesh

Is the off-taste of fish freshly caught in the San Francisco Bay region related to wastes discharged into the bay? The North Bay Water Advisory Council intends to find out. Its study, to be completed by the end of the year, will take three approaches. In one, dilute waste materials will be introduced into untainted fish by intracardial injection; the fish can be prepared and tasted within a few hours. Another approach will use gas chromatographic analysis of the tainted fish. The third will involve growing fish in dilute wastes, then having them tested by organoleptic taste panels.

HEW Sets Atmospheric Areas for Contiguous U.S.

Eight atmospheric areas—segments of the country in which climate, meteorology, and topography are essentially homogeneous—have been designated by the Department of Health, Education, and Welfare, as required by the Air Quality Act of 1967. The areas are delineated mainly on the basis of meteorological data on the occurrence of thermal inversions and on the speed and direction of the winds. They also take into account major topographical features such as the Rocky Mountains. The areas include the Great Lakes–Northeast, Mid-Atlantic Coastal, South Florida, Appalachian, Great Plains, Rocky Mountain, California-Oregon Coastal, and Washington Coastal areas. The basic meteorological data were derived from cooperative research by the National Center for Air Pollution Control of the Public Health Service and the Environmental Science Services Administration of the Department of Commerce. The next step will be in the designation of air quality regions, each of which will have common air pollution problems and require a uniformity of control action. The regions may lie in one or more of the atmospheric areas and may total as many as 100.

1. Mid-Atlantic Coastal Area
2. Great Lakes-Northeast Area
3. Appalachian Area
4. South Florida Area
5. Great Plains Area
6. Rocky Mountain Area
7. Washington Coastal Area
8. California-Oregon Coastal Area

Tall Stacks to Tell All

The effectiveness of tall stacks is going to be determined by measurements in the vicinity of three Pennsylvania Electric Co. plants. The study, undertaken by the National Center for Air Pollution Control, will start with the Keystone Power Station near Indiana, Pa. Effluents from the twin 800-foot stacks will be measured by portable ground station equipment, instrumented helicopters, and devices that use a laser beam. Measurements—principally on sulfur oxides—will be made in each of the four seasons in the coming year. Later, NCAPC will make similar studies on the Homer City Station and the Conemaugh Power Station (near Johnstown), which will have 1000-foot stacks when it begins operation in 1971.

Tall stacks have been used for many years in Great Britain. The Central Electricity Generating Board finds that a stack 2½ times the height of the surrounding buildings can operate for extended periods without adding materially to the general level of pollution, either in the immediate vicinity or in a wider area. Some critics, however, claim that all tall stacks do is disperse pollution to more distant areas.

Conservationists Support Women Voters

The American Conservation Association has given the League of Women Voters a three-year, $30,000 grant to expand the programs of its voters education fund. These programs are aimed at increasing public knowledge of environmental problems, possible solutions, and how citizens can achieve the improvements they want. Since 1965, the league has held six seminars concerning land and water problems in 29 states; six more are scheduled for 1968 and 1969.
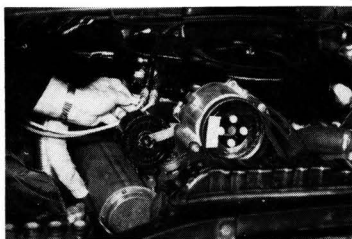
Exhaust Manifold Reactor

The cylinder below the hand is one of two exhaust manifold reactors. The short cylinder just behind the radiator is a pump that feeds air to the reactors

Additional requirements and degrees of control for 1970 model vehicles[a]

Evaporative losses[b]
  Automobiles and light trucks
    6 grams of hydrocarbons per test (90%)

Exhaust
  Heavy trucks and buses
    275 p.p.m. hydrocarbons (35%)
    1.5% carbon monoxide by volume (35%)

  Diesel powered
    20% reduction of light transmission by smoke

[a] For engine crankcase emissions from automobiles and light trucks there is no change from 1968 standards, which require 100% control.

[b] This test simulates evaporation from gas tank and carburetor during one city trip, plus the evaporation caused by expansion and contraction of gas tank vapor during one day.

Comparison of exhaust emissions in new automobiles and light trucks (grams per mile)

	Hydrocarbons	Carbon monoxide
Uncontrolled	9.7	71
1968 standards	3.2	33
1970 standards	2.2	23

Many Act to Curb Vehicle Exhaust Emissions

Exhaust manifold reactors, evaluated by Bureau of Mines (Bartlesville, Okla.), are technically but not yet commercially feasible for reducing automobile exhaust emissions below the levels required by federal standards for all 1968 models. Developed by Du Pont, these reactors mix additional air with exhaust gases to change the gases' chemical properties. As part of BuMines' demonstration car project, these reactors reduced exhaust emissions to the following concentration levels: • Total hydrocarbons to 70 p.p.m. • Photochemically reactive hydrocarbons to 50 p.p.m. • Carbon monoxide to less than 0.7%. • Oxides of nitrogen to 400 to 500 p.p.m.

One reactor showed considerable wear on its inner baffles after 48,000 road miles. But an R&D materials effort concentrating on stainless steels may solve this problem, says Du Pont. Some approaches to the reduction of hydrocarbons and carbon monoxide emissions result in the formation of greater amounts of oxides of nitrogen. However, BuMines' total systems approach using these reactors permits making other adjustments to the engine so that oxides of nitrogen can be reduced to less than 350 p.p.m.

Certifications for 1968 model automobiles reveal that exhaust emission levels are lower than those prescribed by federal standards. Ninety per cent of these models, having engine displacements greater than 140 cubic inches, have been certified with emission levels of 225 p.p.m. hydrocarbons and 1.25% carbon monoxide, lower than the federal standards of 275 p.p.m. hydrocarbons and 1.5% carbon monoxide, according to Dr. John T. Middleton, Director of the National Center for Air Pollution Control. However, although these models meet all federal standards they curtail only 55 to 60% of the total emissions, he cautioned, at the recent hearings on environmental quality of the House Subcommittee on Science, Research, and Development.

Proposed federal standards for 1970 model vehicles include additional items for control and the first step toward uniform regulation of the amount of pollution discharged by a vehicle regardless of its size. Since the development of 1968 standards the National Center for Air Pollution Control has found a more useful relationship between a vehicle's weight and the volume of exhaust discharged by the vehicle per mile. The proposed 1970 standards reflect this relationship and are expressed in terms of weight of pollutant per mile. The proposed 1970 standards limit the discharge to no more than 2.2 grams of hydrocarbons and 23 grams of carbon monoxide per mile for all 11 weight classifications of vehicles. These proposed standards reduce by about one third the 1968 allowable level of pollution from automobiles and require 77% control of hydrocarbons and 68% control of carbon monoxide emissions. For example, under the 1968 standards the Falcon 6 and the Cadillac 8, both in the same engine displacement category of greater than 140 cubic inches, are limited to 275 p.p.m. hydrocarbons emissions. Based on the new NCAPC measure, the Cadillac discharges 4.2 grams of hydrocarbons per mile, the Falcon 6 only 2.5 grams. Under the proposed 1970 standards both cars would be limited to the same discharge, namely 2.2 grams of hydrocarbons per mile. (Also see page 13.)

Science Studies the Far North

The ability of Eskimos to thrive in the Earth's most hostile environment will be studied by a team of scientists from the U.S., Canada, Denmark, and France. With their close relatives, the Aleuts, Eskimos occupy the longest linear distance of any group in the world. Research sites have been set up at four points along the original routes of Eskimo migration—stretching from near Point Barrow to northeastern Greenland. The study, part of the International Biological Program, hopes to gain insights into the general patterns of human adaptability and evolution, patterns that still seem to affect the Eskimo culture.

Science is intruding into another part of the far north, this time to study the ecology of Amchitka, an island near the western end of the Aleutian chain. Reason for the study is that the Atomic Energy Commission is considering the island as a site for underground nuclear tests. The ecological study, to be made by Battelle Memorial Institute, is intended to provide a basis for predicting the possible bioenvironmental effects of the proposed tests and for minimizing adverse effects, whatever they may be. The two main types of hazards to be considered by Battelle are: • The potential biological consequences of physical effects (such as ground motion and water-transmitted shock waves) on fish, wildlife, and their habitats. • The possible transport to man of radionuclides via food chains in the event radioactivity is accidentally released.

Sonic Boom May Not Be Here to Stay

Forward expulsion of electricity by supersonic aircraft could possibly attenuate the sonic boom, according to M. S. Cahn and G. M. Andrew of Northrop Norair (Hawthorne, Calif.). In their paper, "Electroaerodynamics in Supersonic Flow" at the recent Sixth Aerospace Sciences Meeting of the American Institute of Aeronautics and Astronautics in New York City, the two scientists described experimental results, based on small-scale wind tunnel and hydraulic analogy tests, which indicate that electrostatic forces can alter the flow pattern of a fluid. They postulate that if an electrical voltage could be applied to a supersonic aircraft, the oncoming air particles which are charged would be repelled so that the air particles would change their path and flow smoothly around the aircraft, as in subsonic flight. This approach also promises reduction in heat and drag on the aircraft, but the scientists concluded that further research, including wind tunnel tests, would be required before any conclusive data could be obtained.

Meanwhile, don't look for immediate and dramatic reductions in the sonic boom of the current generation of supersonic aircraft, warns a National Academy of Sciences subcommittee. The NAS subcommittee does not rule out the possibility that unconventional aircraft designs may be developed, but feels it more realistic to expect small reductions brought about by better understanding of theory, refinements in aircraft design, and improvements in propulsive efficiency and operating procedures.

National Clean Water Effort Demands More People with Better Skills

Billions of dollars have been spent in recent years in the U.S. for waste treatment facilities—and even larger amounts are due to be spent. For example, federal legislation already on the books authorizes $1.2 billion in 1971 for financial assistance grants to communities for construction of waste treatment facilities.

More plants will require more people—not only more people, but better trained people to operate the larger and more complex plants being built. Personnel shortages already exist, and will grow worse unless corrective action is taken.

So concludes a report presented to the Senate on "Manpower and Training Needs in Water Pollution Control." The report was prepared by the Federal Water Pollution Control Administration in compliance with the Clean Waters Restoration Act of 1966 (ES&T, August 1967, page 601).

Classifying employees

In considering manpower needs, FWPCA classifies personnel into three categories:

• **Professionals.** A great many disciplines are represented—engineers, biologists, chemists, economists, for example—with the range widening as water pollution control problems become more complex.

• **Technicians.** Their duties include, among others, collection of samples, laboratory analysis, and computer programing. Technicians usually have attended technical-vocational schools or junior college.

• **Sewage treatment plant operators.** They are responsible for day-to-day operations. Their training requirements depend on complexity of the plant and are usually satisfied by high school, vocational school, or junior college, plus on-the-job training.

The FWPCA report estimates that 3600 professionals are now employed by state and local agencies. These estimates are highly conservative and exclude replacement needs, FWPCA notes. By 1972, about 9000 should be employed, an increase of 150%. The number of technicians should grow from 2600 to 6500, again a 150% increase. And operators should increase 50%, from 20,000 to 30,000.

But to get these people, state and local agencies will have to compete with other employers in the fields—consulting engineers, industrial waste treatment plants, suppliers of chemicals and equipment for waste treatment plants, other federal agencies, and universities. Looking at some of these needs, FWPCA estimates:

• Consulting engineers, which now account for 6000 professionals and 6000 technicians, will see their needs grow 250%, reaching 21,000 in each category by 1972.

• Industrial waste treatment plants now employ 1700 professionals (about half of whom are chemists, the other half engineers), 1700 technicians, and 3500 plant operators. These plants, which would number 6000 by 1972, will then require 6000 professionals, 6000 technicians, and 12,000 operators—increases of 250%.

Meeting the needs

How will these manpower needs be met? By bolstering efforts in higher education, vocational training, and short-term training. As for professional employees, the FWPCA report compares the current situation in water pollution control with that at the beginning of the space program.

There were few "space scientists" then, but, attracted by the challenges of space, professionals joined the program. If salary levels and employment

**Manpower requirements
for water pollution control**

Professions   Technicians   Plant operators

■ Industrial waste treatment
□ Consulting engineers
■ State and local agencies
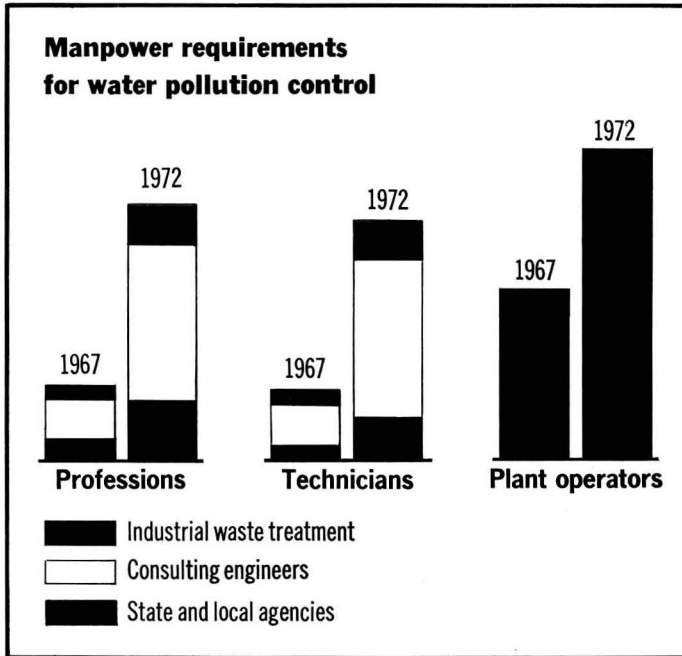
opportunities are competitive, professionals—both new and experienced recruits from allied fields—will join the water pollution control effort.

Both FWPCA and the Office of Water Resources Research (also in the Interior Department) have programs directed at increasing professional personnel. FWPCA's programs include:

• **Graduate training grants,** awarded to institutions to establish or expand advanced education in water pollution control. Funds can be used for stipends to graduate students.

• **Research fellowships,** awarded to individuals for support of graduate and postgraduate training.

• **Research grants,** awarded primarily to support research projects in water pollution control. However, such grants help develop competent professional personnel through indirect support of graduate students.

OWRR's program has provided grant support for establishment of water resources research institutes in 51 land grant colleges. More than 1000 graduate students a year receive financial aid and training as research assistants in projects under way at the various research institutes. In addition, about 14,000 water-study oriented students are enrolled in colleges and universities in the U.S.

Such programs usually take four or five years before they have a significant effect on professional manpower pools. Short-course training can have a more immediate effect, however. Therefore, short-course programs can be used to develop specialized skills in professionals recruited from allied fields, as well as to update the skills of more experienced personnel in the field. FWPCA, for example, offers a series

of such courses based at the Robert A. Taft Sanitary Engineering Center in Cincinnati, Ohio. These courses are being expanded to FWPCA's regional laboratories.

According to the report, "There is probably a sound justification for each professional employee attending at least one week of short-course training per year." However, FWPCA's training courses are projected to reach only about 1000 professionals in fiscal year 1968—and 3600 are currently employed by state and local agencies.

Technicians neglected

FWPCA also offers similar courses for technicians. But in general, little effort has been directed to develop either formal or short-course training programs for the technicians. The report cites two reasons for this lack of effort: the diversity of skills involved and the relatively small number employed by state and local agencies.

FWPCA plans to initiate soon a new program of technical training for subprofessional skills. Under this program, grants will go to technical schools, junior colleges, and similar institutions. The grants will provide funds for teaching staff, equipment, and stipends to trainees. Awards will normally be made to schools in locations with present and future needs for both technicians and sewage treatment plant operators.

The specialized training that technicians and plant operators need may also be developed by other federal programs for vocational and technical training. The report lists five such programs:

• **Manpower development and training** program provides training for unemployed and underemployed persons in both institutional and on-the-job environments. This effort, directed toward reducing skill shortages, offers considerable opportunity for training waste treatment plant operators.

• **Vocational education** program. To take full advantage of the various state programs, water pollution control agencies will have to estimate the quantity of manpower and the quality of skills needed at least two years in advance.

• **Community service and continuing education** program, under the Higher Education Act, provides extremely wide latitude of training and educational activities at subprofessional levels. South Dakota, for example, has already used this program for training sewage plant operators.

• **Community development training** program, administered by the Housing and Urban Development Department, could be used to train state and local government personnel for water pollution control programs.

• **Cooperative Area Manpower Planning System** is an effort to coordinate programs of five federal agencies concerned with technical manpower problems.

Plant operator, the end man

The billions put into sewage treatment plant construction culminate in plants operated by personnel poorly trained and poorly paid. "The result," says the FWPCA report, "is continued pollution of the Nation's water and an unsatisfactory rate of return on the public's clean water investment."

The opportunities for formal training in sewage plant operation are similar to those outlined for technicians. Short-course training, on the other hand, is generally handled by state agencies. In 1966, 8000 operators attended courses offered by 43 states; the type and number of courses offered reflect, to a degree, the size and technical resources of each state. In most cases, however, the courses have not meant improved plant operations, pointing to the need for critical examination of training methods and operator motivation.

The report specifically applauds the training methods of the Missouri Water and Sewerage Technical School at Neosho, which "has developed a worldwide reputation for excellence in its intensive, practical courses in operation of waste treatment facilities." This school receives direct or indirect financial support from state and local agencies, consulting engineers, suppliers of chemicals and equipment, FWPCA, and the Labor Department. This wide support is a contributing factor in the school's success.

Recruiting problems

State and local agencies will need more than training programs to get trained personnel. The new graduate is likely to look elsewhere if salaries are noncompetitive, if positions are filled on the basis of patronage not merit, or if work at the community sewage treatment plant has a low level of prestige and public acceptability. The same is true for plant operators.

Licensing is one effective means of upgrading employment conditions for this group of employees. Licensing, on the basis of demonstrated skills, has the combined effect of improving plant operations and employee status, which provides a better basis for merit system grading of the position. Fifteen states now require licensing of sewage treatment operators.

Still another approach the states might take is to improve productivity of their employees. Some possibilities:

• Review design of sewage treatment plants and pumping stations to minimize maintenance needs and to reduce skill levels required for operation.

• Undertake management studies of employee utilization at all levels to determine how current employees are utilized and to seek maximum use of technicians.

• Seek increased use of automation in design of sewage treatment plants, in sample collection and analysis, in data collection and analysis, and in operation of sewage treatment plants.

Action plan

To assure that adequate supplies of trained manpower are available, FWPCA plans to:

• Continue the orderly expansion of its grant programs.

• Encourage and assist states in emphasizing training aspects of their programs.

• Expand its short-course training programs.

• Develop a cooperative government-wide education and training program to make full use of other federal programs for developing professional and vocational skills.

• Seek to improve the stature and conditions of employment for operators of sewage treatment plants.

• Undertake and support research and development efforts to improve employee productivity.

Copies of "Manpower and Training Needs in Water Pollution Control" are available for 20 cents from: Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

New Procedure Checks Vehicle Exhaust Emissions

Both old and new cars are being tested

so that New Jersey can curb air pollution

from its more than three million cars

A new test procedure and associated testing equipment has been demonstrated for the rapid and low cost evaluation of automobile exhaust emissions. These advances in technology and instrumentation will make available to local, state, and federal authorities the long-sought monitoring system they need for periodic inspection and surveillance. Such regular inspection is essential for major inroads in curbing air pollution caused by automobiles.

Developed by Scott Research Laboratories (Perkasie, Pa., and San Bernardino, Calif.), the test procedure gives information on the composition of automobile exhaust emissions. These data, in turn, provide a basis for determining the proper maintenance program needed to reduce vehicle emissions. Scott's test procedure takes only a minute for a complete analysis and gives data equivalent to those obtained from the lengthier (17 minutes) existing federal procedure that was used to set federal emission standards for 1968 automobiles.

The Scott system employs a set of inertial rolls with a fixed load that serves as external loading to absorb the power output of the automobile. This fixed loading system is inexpensive and requires minimal skill to operate. Yet, data so obtained correlate well with those from the federal procedure. Before settling on the inertial rolls, Scott explored a variety of other external devices including ramps and dynamometers.

Federal procedure

Used to establish emission standards for 1968 automobiles, the federal procedure consists of a prescribed sequence of vehicle operating conditions on a chassis dynamometer. The exhaust gases are sampled continuously through an analytical train. The basic test is designed to determine hydrocarbons and carbon monoxide concentrations for an average trip in a metropolitan area of 17 minutes from a cold start. The test has two parts: four seven-mode warmup cycles and three seven-mode hot cycles (the fifth cycle is not read). The average concentrations for the warmup cycles and the hot cycles are combined to yield the overall emission value for the car.

This federal test procedure yields values for hydrocarbons and carbon monoxide concentrations from a tested vehicle or engine for comparison with the standards. However, the finding that the vehicle or engine operates within the standards is not judged on the basis of a single vehicle or single engine. Performance is judged on the basis of emissions of groups of test vehicles.

Proposed loading device

Rolls
Lift
Floor level
Fixed inertia
Fixed power absorber
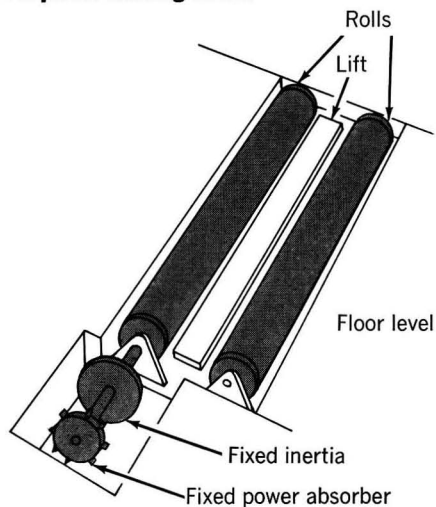
Comparison of ACID cycle with 7-mode cycle
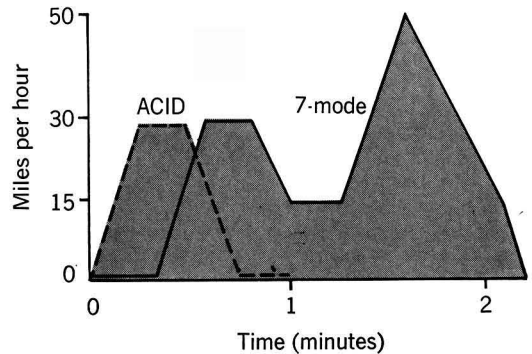
Based on data from 20 to 30 vehicles, each having a road life of 50,000 miles, emission standards for 1968 automobiles having a displacement greater than 140 cubic inches were set at 275 p.p.m. hydrocarbons and 1.5% carbon monoxide by volume. Costs for such a testing program run about $200 per test.

Scott's procedure

The vehicle is driven on the dynamometer, which is set for 3000 pounds of inertia with the horsepower equivalent to 11 at 50 m.p.h. With the appropriate sampling devices attached to the vehicle, the driver twice depresses the accelerator half-way to the floor with the transmission in neutral. Then he puts the transmission to drive for automatic transmissions or low for manuals, and immediately drives the following ACID cycle once, shifting on acceleration at 15 and 25 m.p.h. for manual transmissions.

ACID cycle

Of the several test emission cycles that Scott tested and compared with the federal seven-mode test, a one-minute four-mode cycle gave good correlation. Corresponding to the four modes of operation—Acceleration, Cruise, Idle, and Deceleration—ACID places the modes of operation in order of decreasing importance as established in the seven-mode federal cycle. The ACID cycle was developed through the help of a computer study that used a multiple regression technique to analyze data from several hundred seven-mode tests.

Sample collection and analysis

The preferred method of collecting a sample of exhaust gas uses a variable dilution technique, expected to be used in the standard method to be proposed by the Federal Government later this year. In this method a blower is attached to a large diameter tube which leads to the exhaust and fits it very loosely. The flow rate is constant yet great enough to collect all of the exhaust under the most extreme conditions to be used. Ambient air makes up any volume difference. After exhaust and air have thoroughly mixed, a constant mass flow sample is withdrawn for analysis. In addition to its low cost, this method has the added feature of removing exhaust fumes from the inspection station.

The analytical system consists of a flame ionization analyzer for hydrocarbons and nondispersive infrared analyzers for carbon monoxide and carbon dioxide. (A catalytic combustor is provided before the carbon dioxide analyzer.) In operation, each analyzer completes its cycle in less than 15 seconds.

Crankcase emission and smoke test

In the method for analysis of crankcase emissions, a tube is connected to the crankcase compartment. A pump draws a known and constant volume of gas out of the crankcase compartment. This volume of gas is greater than any possible blowby volume. While the vehicle is driven through the exhaust test cycle, the gas mixture is analyzed for hydrocarbons. The analysis is directly proportional to emissions because the sampling rate is constant and known.

For the smoke test an opacity smoke meter is placed on the variable dilution duct where the meter measures maximum smoke opacity or density. Although this test is not required by present federal standards, it is required by the state of New Jersey and is included in proposed 1970 federal standards.

Legislation

In 1966 the state of New Jersey authorized its Department of Health to set standards for automobile exhaust emissions. New Jersey may well become the first state in the nation to control and regulate the exhaust emissions from its automobiles—more than three million registered. The New Jersey law, which will become effective this fall, requires the Department of Health to set emission standards for all motor vehicles, including cars, buses, trucks, and the like. Most importantly, the law includes both old and new vehicles.

Under a federal demonstration grant from the National Center for Air Pollution Control, for which 75% of the funding was available from the Federal Government, the N.J. Department of Health awarded a two-year contract totaling $400,000 to Scott Research Laboratories to develop a rapid low-cost diagnostic test for exhaust emissions from automobiles. It was this project that led to this new test se-

ACID cycle vs. 7-mode cycle

Carbon monoxide (%), ACID cycle[a]
Probe/mode calculation

Probe/mode calculation
Carbon monoxide (%), 7-mode cycle[a]
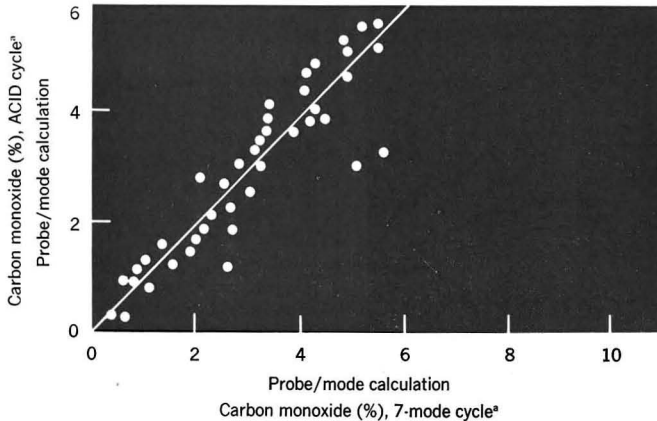
[a]Corrected and weighted

Federal standards for exhaust emissions

For new (1968) motor vehicles and motor vehicle engines

Cylinder displacement (cubic inches)	Hydrocarbons (p.p.m.)	Carbon monoxide (per cent by volume)
50–100	410	2.3
100–140	350	2.0
>140	275	1.5

Source: Federal Register

ACID cycle vs. 7-mode cycle

Hydrocarbons (p.p.m.), ACID cycle[a]
Probe/mode calculation

Probe/mode calculation
Hydrocarbons (p.p.m.), 7-mode cycle[a]
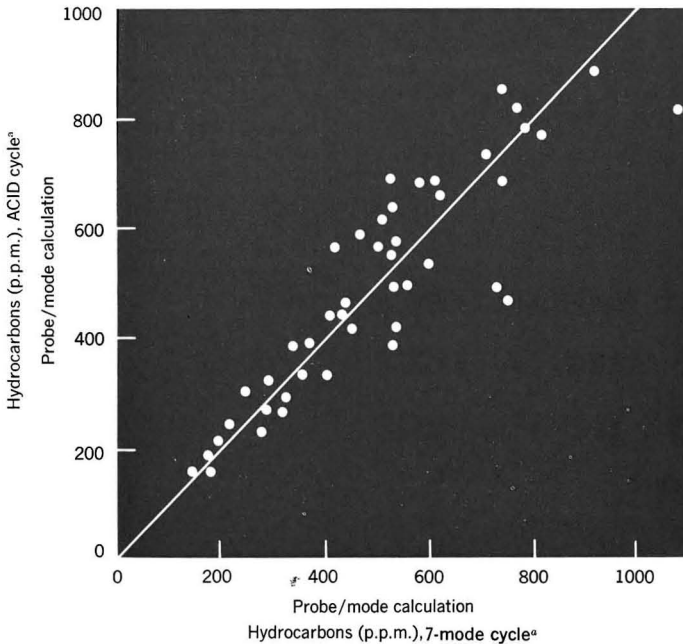
[a]Corrected and weighted

quence and equipment that takes one minute to complete at a cost of 30 to 40 cents per test.

Development

In Phase I (December 1966–July 1967), two prototype exhaust emission testing units were developed by Scott. Data from these units were compared with data on the already established federal standards. These prototype units also had provision for smoke determinations, as required by the New Jersey statute, and possibly by the 1970 federal standards.

Phase II consists of testing the proto-type unit on a sample of vehicle representative of the vehicle population in New Jersey. Phase III will be used to test the equipment in California. Phases II and III are being conducted concurrently and should be completed in March.

Phases II and III were initiated last August. Using one of the prototype units located at a test site in Trenton, Scott will obtain data on some 200 vehicles within New Jersey. At the same time, Scott will obtain data on another 200 vehicles at a test site in California. Scott will give the results of both the New Jersey and California tests (Phases II and III) to the New Jersey Department of Health. These tests should provide reliable information on levels of exhaust emissions for pre-1968 New Jersey automobiles sans control devices, pre-1966 California automobiles having an additional two-year road life, as well as intermediary 1967 California automobiles, and new 1968 California automobiles. Cali-
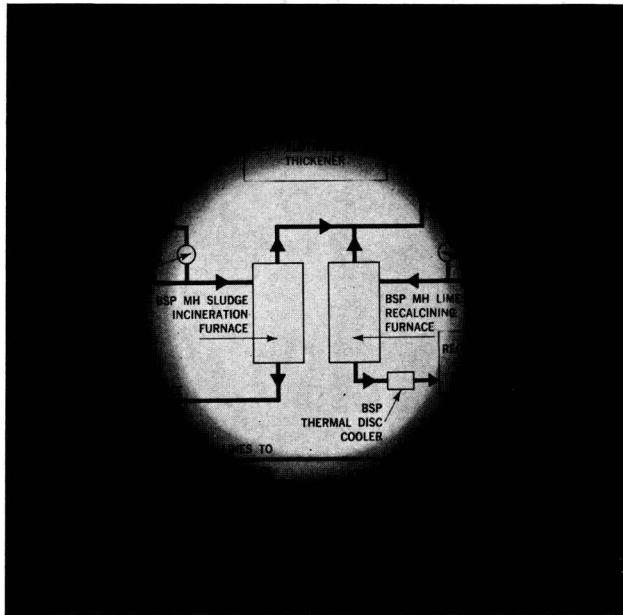
TAHOE: The inside story

Funded in part by the F.W.P.C.A. and E.D.A., the second phase of the world's most advanced waste treatment facility is now under way. Bartlett-Snow-Pacific will provide the solids handling system, including primary/secondary sewage sludge incineration and secondary/tertiary lime sludge regeneration. During the first phase, B-S-P supplied multiple hearth carbon regeneration equipment for economical carbon adsorption filtration.

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fornia has required automobiles to have both exhaust and crankcase control devices since 1966.

Second generation prototype unit

A second generation unit, really a modification of the basic prototype units, permits mass analysis rather than concentration analysis as in the early units. The mass analysis feature has been incorporated in the setup as an aid to the instrumentation. Furthermore, mass analysis should help in measuring pollutants in the new units (grams per mile) proposed for the 1970 federal standards.

New Jersey time schedule

New Jersey has a system of state-operated safety inspection stations for motor vehicles. Installation of the new emission test equipment at these stations should provide a means for controlling the state's pollution problem caused by automobile exhaust. In this manner, both old and new vehicles, already subject to safety inspections by New Jersey's State Board of Motor Vehicles, can be made to meet the emissions standards that will be set by the state's Department of Health before the vehicle is allowed to operate in the state.

Most likely, the New Jersey Department of Health will place a production contract on open bid for at least 78 testing units—one for each of its state-operated safety inspection stations. A conservative estimate places the cost of each unit at $10,000, for a total production contract of about three quarters of a million dollars.

Data from Phases II and III will point out what qualitative and quantitative effects a tune-up of an old engine has on its exhaust emission patterns. After the data have been evaluated by the New Jersey Department of Health, a public hearing will be convened, probably in the fall of 1968, so that the data can be presented and all interested parties heard. By that time some of the 78 test units should be available. In all, New Jersey authorities estimate that more than three million cars will be evaluated in the state. And that in all probability the number of tests will approach the four million mark because of repeats and evaluations for tune-ups and the like.

Bringing Potable Water to Some Have-Not People

In six years, the Alliance for Progress has brought potable water (and in some cases sewage systems) to 55.6 million Latin Americans— but a formidable job is still to be done
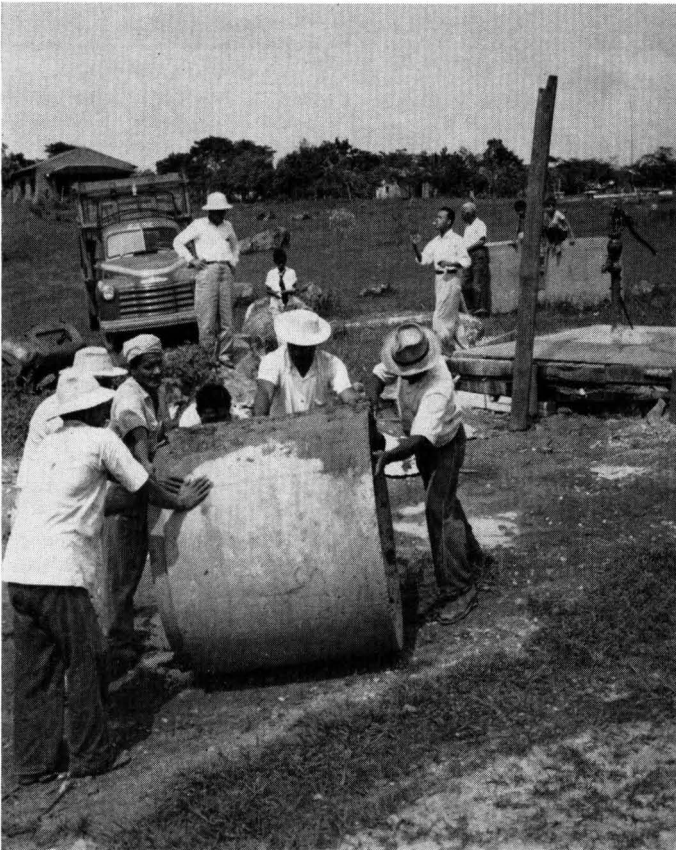
Well digging. *Villagers near La Chorrera, Panama, are able to sink their own wells by forming neighborhood committees, raising funds through social activities such as movies, lotteries, and fiestas, and working under the guidance of the Public Health Department. Here workers roll a concrete liner into place.*

"To provide adequate potable water supply and sewage disposal to not less than 70% of the urban and 50% of the rural population during the present decade . . ."

This was one of the goals of the Charter of Punta del Este (1961) which set up the Alliance for Progress. It was reaffirmed early last year in the Declaration of the Presidents of America, signed by the American chiefs of state at their meeting in Punta del Este, Uruguay.

Six years of that decade are past. In his Washington office recently, Dr. Mark D. Hollis, chief engineer, Pan American Health Organization–World Health Organization, assessed for ES&T, the progress made to date on this goal, which involves reaching about 150 million people in Latin America. His assessment: The water objective will probably be met for the urban population, but efforts will have to be stepped up considerably to do so for the rural population. As for sewage systems, the urban centers are moving along in good order. However, on a continental basis, the program of sewage disposal is just getting under way. But the achievement in providing water supplies has produced, in most countries, the organizational structures, administrative capabilities, and technical methods that can accelerate the entire sewage program.

Thus, portions of the goal may not be achieved. Still, the overall achievement is considerable—55.6 million people obtained potable water in six

Homeward trek. *After waiting in long queues for many hours, the inhabitants of this village of 25,000 in Peru carry their precious water home. The water is available from only three small pipes which deliver water, under very low pressure, for only three hours on only three mornings each week*

Water mains. *To increase the supply of water, villagers lay water mains in the rural village of Poa, State of Yaracuy, Venezuela*

If a single program were chosen which would have the maximum health benefits, which would rapidly stimulate social and economic development, and which would materially improve the standard of living of people, that program would be water supply with provision for running water into or adjacent to the house. "Facts on Health Problems," Pan American Health Organization

years. It was a cooperative effort all the way. The people (through their governments) put their talents and money ($723.5 million to date) behind the projects; PAHO lent technical assistance: and the international banks (principally the Inter-American Development Bank) extended loans totaling $534.6 million.

Crucial to all of this, as Hollis sees it, is involvement of the local populace. "When it's their money, their people, their institutions, projects are likelier to be set up properly and maintained properly once they are set up," he notes.

PAHO's resources for the water and sewage disposal program are about $2

Latin America's water supply much improved in cities, but still needs much improvement in rural areas

Haiti
0.8 (17%)
3.9

Mexico
24.7 (81%)
20.7 (18%)

Cuba
5.0 (90%)
2.9 (60%)

Dominican Republic
1.4 (58%)
2.5 (8%)

Guatemala
1.7 (82%)
3.0 (10%)

Honduras
0.7 (91%)
1.8 (11%)

Jamaica
0.5 (98%)
1.4 (62%)

Barbados
0.1 (100%)
0.1 (88%)

El Salvador
1.2 (80%)
1.8 (28%)

Nicaragua
0.8 (78%)
1.0 (4%)

Venezuela
5.9 (88%)
3.4 (50%)

Trinidad and Tobago
0.4 (100%)
0.6 (95%)

Costa Rica
0.7 (100%)
0.8 (48%)

Panama
0.6 (91%)
0.7 (18%)

Colombia
10.4 (85%)
8.7 (49%)

Guyana
0.2 (100%)
0.5 (60%)

Ecuador
2.0 (73%)
3.4 (8%)

Brazil
46.2 (49%)
40.2 (14%)

Peru
5.8 (59%)
6.4 (7%)

Bolivia
1.5 (55%)
2.5 (1%)

Paraguay
0.8 (16%)
1.4 (1%)

Chile
6.4 (83%)
2.6 (2%)

Argentina
16.4 (72%)
6.8 (5%)

Uruguay
2.3 (82%)
0.5 (12%)

Other Caribbean Countries
0.6 (77%)
0.7 (65%)

Totals 137.1 (66%)
118.5 (19%)

All population figures in millions.
Numbers in black show urban population;
those in parentheses show the percent served
by house connection or public hydrant.

Numbers in color show rural population;
those in parentheses show the per cent served
by house connections or public hydrant.

Community water supply program in Latin America

Funds for first six years of the Alliance Decade (1961–71)

National funds $.724 billion

International loans $.535 billion

$1.26 billion

Urban programs $1.05 billion

Rural programs $.214 billion
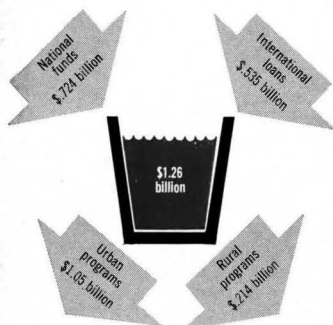
Public fountain. *Because their homes have no running water, villagers fetch water from a public fountain in San Jorge, Guatemala, a rural village like myriad others where 63% of the population in Central America and 58% of the population in South America live with hope of better days*

million annually. Early in the game PAHO realized that getting enough local professionals was a problem. Therefore, one of the first moves was to shore up the engineering departments of the 50 or so universities in Latin America.

Now the health organization has agreements with more than 30 universities. These agreements cover such things as:

• Hiring consultants for reviewing or starting educational programs.

• Providing advisory services for improving physical facilities or for preparing requests to financing agencies.

• Establishing fellowships for the teaching staff.

• Initiating short courses.

• Promoting research.

Still another way PAHO has helped is in setting up national or provincial authorities empowered to plan, organize, construct, manage, and finance water systems. These strong administrative structures, PAHO believes, will lead the way to the improvement of other aspects of environmental health in Latin America.

Water first

When it comes to actually starting the projects, PAHO feels that potable water supplies should come first. "We're approaching the problem the way it was done in the U.S. in the

1930's—only we're doing it much faster," Hollis says. "Starting the effort with water for the cities was the quickest way to reach large numbers of people, as well as the easiest way to develop the know-how needed to push the program on into the rural areas."

Some other parts of the world are trying to develop water supplies and sewage disposal hand in hand. Funds are not always available to do this, Hollis points out. "Besides, we feel there's just nothing more basic than water. And that job alone was tremendous when you consider that in 1961 almost no cities in Latin America had water under pressure 24 hours a day, seven days a week."

The results to date in Latin American cities are impressive. Of 137.1 million people, 90.6 million, or 66%, now have water supplies, either from house connections or nearby public hydrants. (The figure for the entire Latin American population is 44%.) Thus, the 1971 goal of 70% should easily be met, Hollis believes. Indeed, 19 countries have already done so.

The rural population is another matter, and progress for this group is urgent. "We must reduce the contrast between the amenities in urban and rural areas," according to Hollis. "It will help stem the rush to the cities. At the same time, it will strengthen the agri-

cultural economy and bring more social stability."

Of the 118.5 million people in rural areas, 22.6 million, or 19% are being served with potable water. Yet, another 37.1 million will have to be served in the next four years to meet the Alliance decade goal of 50% for the rural areas. Eight countries have already met the goal.

Getting water to these countless small communities will require new approaches, according to Hollis. One approach under consideration was described at the Water for Peace Conference by Harvey F. Ludwig and Alfred W. Jorgensen of Engineering-Science, Inc. The approach involves standardizing methods for engineering, installing, and maintaining rural water systems.

In practice, the approach works this way: an engineer in a central office works from photographs showing the community and its environs, including sources of water supply. (This procedure eliminates expensive and time-consuming field surveys.) He then turns to a design manual, one of three manuals specially prepared for this kind of approach, and selects the standardized package module that fits the study area and population. He assembles the equipment and supplies needed from a catalog, also specially prepared.

The package is delivered as a unit to the village, where it is installed by local personnel, following illustrations and step-by-step directions in the installation manual. An operation and maintenance manual is also provided, again highly simplified, to permit personnel of limited technical training to operate, maintain, and repair the system.

Sewage disposal

The remainder of the Alliance for Progress decade will stress the rural areas and sewage disposal. Whereas water supply has been approached on a national basis, sewage disposal has been case by case. PAHO plans to keep the management and financing of water supplies and sewage disposal in one organization. According to Hollis, "We want to avoid the two organization system that developed in the U.S. In the 1930's, water bonds had no trouble getting popular support, but as many as half the sewage treatment bonds were turned down. Water in and sewers out should be considered a package."

These figures give the scope of the job still to be done: 53% of the urban population lives in houses connected to a sewage system. Only Uruguay has reached the charter goal of 70%. Only five countries exceed the 53% average for all Latin America.

Very little headway has been made on the rural population. Here again, says Hollis, "We may have to come up with some new approaches to reach the small rural communities. But with the momentum the water program has given to these communities, plus the organizational structures established, we may still see substantial progress on the rural sewage problem."

"And when these traditional sanitation problems are under better control, we will be faced—and, of course, we are to a degree even now—with the urbanization and industrialization problems already plaguing the U.S. and other more developed countries."

ENGINEERING FOR HUMAN FULFILLMENT

Clearly our first target in dealing with man's environment is to make it safe—as free as possible of specific hazards. I am not suggesting that we try to create a world totally free of risk. That would be not only impossible of achievement but very possibly detrimental to man's long-range growth. Rather, I am suggesting that no man or population group should be compelled to expose themselves to preventable risk of disease or disability, as a condition of employment or as a condition of urban living. This is a fair goal. It is also a minimal goal.

Yet we don't have to look very far to discover that we are a long way from achieving this minimum. The air over our cities is filled with substances known to be dangerous. Thousands of workers in dozens of industries place their health in jeopardy when they punch the clock in the morning. Through the water we drink, the food we eat, and the air we breathe, we are ingesting minute quantities of substances from arsenic to zirconium, day by day, throughout a lifetime. No one can yet say with any certainty what the cumulative effect may be. Meanwhile we already know how to remove a great many of these substances from our surroundings. What is lacking is the firm social decision to do it. This decision will not be made by professionals; it belongs to society at large.

One way by which professionals can affect the decision is to enlarge the concept of health. It is out-of-date to think of health solely in negative terms—as the absence of disease and disability. The healthy individual is not merely unsick. He is strong, aware of his powers, and eager to use them. Therefore, in our approach to the environment we need to be conscious of sanity as well as sanitation. We should be as concerned with ugliness and loneliness as we are with carcinogens. The truly healthful environment is not merely safe but stimulating. This is a much higher goal than mere freedom from definable hazard. But by shooting for it we shall, I think, rally to our banner many people for whom the negative objective is not worth the effort.

It seems to me that we urgently need a major effort in what might be termed "engineering for consumption." Consider, for example, the problem of solid wastes which is plaguing every city and blighting much of our countryside. Every day our urban communities produce 800 million pounds of solid wastes. Every year we spend upwards of $3 billion to collect and dispose of this accumulation. There is no limit in sight, either to the production of wastes or to the cost of getting rid of them.

Yet the basic technologies for waste collection and disposal have remained relatively unchanged during a quarter-century in which the size of the problem and its visibility have magnified enormously. The same old methods are still in use—incineration, landfill, composting, salvage, and reclamation. They have been studied here and there, refined in certain ways. Occasionally they are put to imaginative use. But if there has been a real advance, it is much better hidden than the refuse.

Dr. William H. Stewart

Surgeon General, Public Health Service, U.S. Department of Health, Education, and Welfare, at the Third Annual Meeting of the National Academy of Engineering, Ann Arbor, Mich., Sept. 21, 1967.

Air quality program needs uniform tests

With increasing emphasis on establishing and policing air quality regulations throughout the U.S., experts see a real need for standard, professional-approved laboratory methods

The accelerating pace of air pollution control activities has intensified the need to examine critically the methods of measurement. Methods of air analyses are the basic tools for studying air pollution processes and effects, for monitoring the present degrees of pollution, for setting air quality standards, and for evaluating control efforts. Collaborative testing of proposed procedures is the essential final step before the procedures can be accepted as standard methods. This article outlines the objectives of the standardization program, the present activities, and plans for future work.

Many experts have reviewed the unfilled needs in the field of air pollution measurements. And many states and organizations have established criteria and standards. For example, California has recognized standardization of methods as a principal aim for many years. The First Conference on Methods in Air Pollution Studies was held in 1958 under the sponsorship of the California State Department of Public Health. The purpose of the conference was to exchange information on methods and techniques, to discuss critically their practicality and the limitations on interpretation of results, and to standardize methods. In the keynote address for the seventh of these conferences, which was held in Los Angeles in January 1965, Mr. Clifton J. Seymour, Air Pollution Control Officer for Riverside County, emphasized that standard methods were needed for state air quality standards:

"Have we come up with recommended procedures for methods and techniques used in calibration of automatic atmosphere analyzers and analytical methods used for pollutants, has any extensive research been done on practicality of the various methods and instruments for laboratory or field use, has any definite limitation been set on interpretation of results from sampling of the common air pollutants? It is very unfortunate, but the answer is an emphatic 'no'."

The World Health Organization's "Methods for Measuring Air Pollutants—A Draft Report" recognized the same problem. The report was prepared in 1965 with the assistance of Dr. Morris Katz and will be issued soon. The report notes:

"Where it is possible or expedient to employ several methods for the characterization of a specific or nonspecific air pollutant, the relation between these methods in terms of appropriate conversion factors must be known. Only by such means can the results of work in different countries be compared."

Enforcement experience

Much can be learned from experience in other enforcement activities. The Food and Drug Administration, after early defeats in the courts, decided to allocate substantial portions of its funds for testing of laboratory methods and for promulgation of standard methods. FDA recognized belatedly that calling a method a standard method was not sufficient; the actual supporting evidence was required in court.

A similar experience befell the Public Health Service's Division of Water Supply and Pollution Control in prosecution of a case involving fish kill in the lower Mississippi River. One defense of the Velsicol Chemical Corp., which PHS accused as being a major polluter, consisted of an attack on the validity of the analytical work done by PHS.

Large organizations can probably litigate a few cases through the courts without benefit of standard laboratory methods. provided that recognized experts are available to testify and that a substantial amount of supporting laboratory data is prepared. When the number of cases expands to tens and hundreds, however, and when some of these cases also involve smaller industries and state and local agencies, the only practical approach is to use standard laboratory methods approved by a recognized professional organization. Past experience has shown that the courts accept this practice, especially if certified laboratories and chemists conduct the tests. The possibility of 50 sets of regulations emphasizes the need for national standard laboratory test methods.

Many organizations

A variety of organizations engage in activities directly or indirectly related to methodology for air pollution measurements. The American Society for

FEATURE

Bernard E. Saltzman

Department of Environmental Health, University of Cincinnati, and retired deputy chief of the
Chemical Research and Development Section, Division of Air Pollution, PHS, Cincinnati, Ohio

Testing and Materials, Committee D-22, presented 14 methods in the manual "ASTM Standards on Methods of Atmospheric Sampling and Analysis" (second edition, 1962). This committee consists of about 75 representatives of governmental, institutional, and industrial organizations. ASTM has developed a well established procedure for approval of methods by letter-ballot and for their publication. Its standard methods for materials have been tested and have received wide recognition in certain industrial fields. However, there has been only limited laboratory testing of its air pollution procedures.

The American Conference of Governmental Industrial Hygienists has maintained a Committee on Recommended Analytical Methods since 1944. This committee has issued a manual describing 18 procedures, all collaboratively tested; the first of these were approved in 1949. Most are for concentrations encountered in industrial hygiene work, levels that may be 100 times or more higher than those of air pollution interest. The committee's activity has been retarded by the volunteer nature of the work and by the lack of adequate funding and recognition by participating groups.

Other organizations have also collected analytical methods. Among them: American Industrial Hygiene Association, American Petroleum Institute, Manufacturing Chemists Association, Air Pollution Control Associa-

Table 1
Classification of responding laboratories[a]

Location	Number responding					
	Governmental			University, testing laboratory or research organization	Industrial	Total
	Federal	State	Local			
Alabama	1	1	1			3
California		1	4		3	8
Colorado		1		1		2
Connecticut		1			1	2
District of Columbia	1		1			2
Florida	1				1	2
Hawaii		1				1
Idaho					1	1
Illinois		1			5	6
Indiana		1			1	2
Kentucky		1	1			2
Maryland			1			1
Massachusetts		1		1		2
Michigan		1	1		2	4
Missouri					1	1
New Jersey				1		1
New York		1		3	1	5
Nevada			1			1
North Carolina			2			2
Ohio	6	1				7
Oklahoma		1	2			3
Pennsylvania	1	1		1	2	5
South Carolina	1					1
Tennessee		1				1
Texas		1				1
Utah	1				1	2
Virginia					1	1
Washington		1		1	1	3
Wisconsin			1			1
Foreign	2	1		1	1	5
Totals	**14**	**18**	**15**	**9**	**22**	**78**

[a] Reports received before April 25, 1967.

tion (through its technical manuals), Los Angeles County Air Pollution Control District, California State Department of Public Health, Organization for Economic Cooperation and Development (Paris), and World Health Organization (Geneva).

Relevant publications of the PHS National Center for Air Pollution Control are "Air Pollution Control Field Operations Manual" prepared in 1962 by the Los Angeles County Air Pollution Control District (Weisburd, 1962), "Methods of Measuring and Monitoring Atmospheric Sulfur Dioxide" (Hochheiser, 1964), and "Selected Methods for the Measurement of Air Pollutants" (Interbranch Chemical Advisory Committee, 1965).

All these collections were made in an informal manner, with no claim of formal collaborative laboratory testing. Comparisons indicate a variety of overlapping and differing procedures.

Intersociety Committee

In April 1960, representatives of several national societies unanimously adopted the following resolution:

"There is need for compilation of recommended methods of air sampling and analysis over and beyond current activities in the field and for coordinating a more rapid action on evaluation of methods."

As a result of this resolution and subsequent deliberations, the American Public Health Association, on behalf of six societies, applied for and received a grant in 1963 from PHS for development of a Manual of Methods for Ambient Air Sampling and Analysis. A seventh society later joined the group.

The Intersociety Committee comprises the following:

• Air Pollution Control Association (Dr. E. R. Hendrickson, chairman and principal investigator).

• American Conference of Govern-mental Industrial Hygienists (Mr. R. G. Keenan).

• American Industrial Hygiene Association (Dr. Allen D. Brandt).

• American Public Health Association (Dr. Leonard Greenburg).

• American Society for Testing and Materials (Mr. Paul Giever).

• American Society of Mechanical Engineers (Mr. Arthur C. Stern).

• Association of Official Analytical Chemists (Dr. Bernard E. Saltzman).

• Co-principal investigator (Dr. George J. Kupchik of APHA) and editor (Dr. Moyer D. Thomas).

Eight substance subcommittees were organized in 1966 to cover the various categories of pollutants; each subcommittee consists of representatives from the seven societies. These subcommittees will recommend methods of analyses to be reviewed by the editor and approved by the Intersociety Committee. After approval a procedure will be published as a tentative method. At this stage the procedure will be referred to the collaborative testing coordinating organization set up in July 1966 by the PHS Division of Air Pollution (now the National Center for Air Pollution Control). The testing group, known as the Analytical Methods Evaluation Service, seeks the following:

• Development of technology for the collaborative testing of methods of air sampling and analysis.

• Application of identical sampling and analytical methodology by a group of collaborating laboratories. The groups use identical methods of gaseous or aerosol sample preparation to establish the reproducibility of a published method in the hands of different chemists in different laboratories.

• Optimization of these sampling and analytical methods before or after their collaborative testing, including the minimizing of the effects of interfering substances.

The Analytical Methods Evaluation Service will work in close cooperation with the Intersociety Committee on Manual of Methods for Ambient Air Sampling and Analysis, and will give first priority to testing the committee's methods. Results of the collaborative tests will be forwarded to the committee and also will be published.

National survey

As a first step the Analytical Methods Evaluation Service published a questionnaire inviting laboratories to submit information on the methods and instruments currently in use and to indicate their interest in participating in collaborative testing. Tables 1 through 9 summarize the responses. They indicate a pattern of present usage of methods that suggests an order of priority in importance. Almost all laboratories indicated their willingness to participate in collaborative testing.

Table 1 shows that close to 80 laboratories responded from 28 states and three foreign countries. In 1966 V. G. Mackenzie of the National Center for Air Pollution Control told a Congressional committee that 33 states had air pollution programs, although many programs were nominal. In 19 states the agencies had abatement responsibilities, but only a half dozen engaged in more than nominal abatement activity. Thus, the 17 state agencies responding to our survey represent a large portion of this group.

Mackenzie also indicated that there were 130 local air pollution programs, 62 of which were five or more years old. We received 15 responses from local governmental agencies.

It is difficult to estimate the number of active laboratories in the nongovernmental categories. However, the responses are a significant, although not necessarily representative, sample of what is being done.

Tables 2 through 7 summarize continuous monitoring instruments in use

<div align="center">

Table 2
Continuous monitoring instruments in use for sulfur dioxide in ambient air[a]

</div>

Type	Number of labs possessing instrument	Number of instruments	Remarks by laboratories on performance[b]
Conductometric:			
Leeds & Northrup Co. (Thomas Autometer)	11	38	(2,1,1,1) no comment; (10,2) good; (1) satisfactory; (2) adequate; (16) fair, not good at <0.1 p.p.m.; (1) heavy maintenance; (1) erratic, trouble with bubbles
Davis Emergency Equipment Co.	9	13[c]	(1[c],1,1,1,1) no comment; (1) excellent; (1) good; (1) Model 11-7010, no comment; (5) Model 11-7010, good, question low values
Beckman Instruments, Inc.	4	12	(3,1) no comment; (6) good; (2) slow response to change in concentration
Instrument Development Co.	6	8[c]	(1[c],1,1) no comment; (1) good; (3) OK, bad features include no temperature compensation and 30-minute integrated sample; (1) questionable
Scientific Instrument Co.	2	3	(2) no comment; (1) excellent in operation, ease of calibration, portability, and reagent requirements
Industrial Scientific Research Corp.	1	3	(3) fair
Scientific Industries, Inc.	1	1	(1) good
Homemade or unspecified	3	10	(6,3) no comment; (1) not accurate below 0.5 p.p.m.
Colorimetric:			
Precision Scientific Development Co.	3	4	(2) no comment; (1) solution pump very poor; (1) excessive maintenance required
Technicon Controls, Inc.	1	1	(1) no comment
Kimoto Electric Co. (Japan)	1	1	(1) no comment
Wilkens-Anderson Co.	1	1	(1) excellent (by manufacturer)
Coulometric:			
Beckman Instruments, Inc.	2	4	(3,1) no comment
Bell and Howell Co. (CEC-Titrilog)	2	2	(1) no comment, (1) hard to maintain
Miscellaneous:			
Barringer Research, Ltd. (spectrophotometric)	1	1	(1) specific (by manufacturer)
Gas Chromatography (S. Africa) Model 65-8	1	1	(1) satisfactory
Any type	39[d]	104[c]	
Method of standardization:			
H_2SO_4	14	28	
SO_2 gas	16	26[c]	
H_2SO_4/SO_2	6	28	
SO_2 permeation tube	3	4[c]	
$NaHSO_3$, $Na_2S_2O_5$	4	5	
Calibrated optical filters	1	1	
Electronic	1	1	

[a] Reports received before April 25, 1967.
[b] Number of instruments of this type possessed by the laboratory making this comment is indicated in ( ). Thus (10,3) denotes that this remark was made by two laboratories, having 10 and 3 instruments, respectively. Validity of the comments was not investigated.
[c] Number may be greater; only one instrument of each type was credited to some laboratories not indicating number.
[d] This number is less than the sum of the preceding items because some laboratories have more than one type of instrument.

Table 3
Continuous monitoring instruments in use for oxidant (including ozone) in ambient air[a]

Type	Number of labs possessing instrument	Number of instruments	Remarks by laboratories on performance[b]
Coulometric:			
Mast Development Co.	16	37	(2,1,1,1,1,1,) no comment; (5) excellent; (8) good; (5) good but some problems; (2) fair to good; (1) fairly satisfactory; (1) satisfactory; (1) requires very careful preconditioning; (1) three breakdowns in six months; (5) variable, inconsistent; (1) marginal
Wellsbach Corp.	1	2	(2) fair
Beckman Instruments, Inc.	2	4	(3,1) no comment
Colorimetric:			
Beckman Instruments, Inc.	7	26[c]	(1) no comment; (11) good; (1) good in lower ranges; (6,1[c]) fair; (1) fair, but readings are a little low; (5[c]) continued maintenance and periodic calibration required
Harold Kruger Instruments[e]	3	8[c]	(3) excellent but large; (1) trouble free; (4[c]) continued maintenance and periodic calibration required
Homemade	1	1	(1) excellent
Any type	26[d]	78[c]	

Methods of standardization:

Almost all laboratories use dynamic systems employing ozone lamps and wet analysis with neutral KI reagent. Chlorine and iodine were also mentioned.

[a] Reports received before April 25, 1967.
[b] Number of instruments of this type possessed by the laboratory making this comment is indicated in ( ). Thus (10,3) denotes that this remark was made by two laboratories having 10 and 3 instruments, respectively. Validity of the comments was not investigated.
[c] Number estimated; some laboratories did not exactly specify numbers and types.
[d] This number is less than the sum of the preceding items because some laboratories have more than one type of instrument.
[e] No longer manufactured.

Table 4
Continuous monitoring instruments in use for hydrocarbons in ambient air[a]

Type	Number of labs possessing instrument	Number of instruments	Remarks by laboratories on performance[b]
Flame Ionization:			
Beckman Instruments, Inc.	9	31[c]	(10,2,1,1) no comment; (8,5,1[c],1) good; (2) unsatisfactory so far, constant drift;—(3,3,1) used with carbon tube as methane analyzer
Power Design, Inc.	3	20	(1) excellent; (6) good; (13) adequate
Varian Aerograph (Wilkens)	1	1	(1) satisfactory
Homemade	1	3	(3) excellent
Any type	14	55[c]	

Methods of Standardization:

Almost all laboratories use tank gas for zero and span (either methane or propane).

[a] Reports received before April 25, 1967.
[b] Number of instruments of this type possessed by the laboratory making this comment is indicated in ( ). Thus (10,3) denotes that this remark was made by two laboratories having 10 and 3 instruments, respectively. Validity of the comments was not investigated.
[c] Number may be greater; only one instrument of each type was credited to some laboratories not indicating number.

for ambient air analysis. The pollutants being analyzed, arranged in decreasing order of number of operating instruments, were the following: sulfur dioxide, dust and hydrogen sulfide (tape samplers), oxidants, hydrocarbons, nitrogen oxides, carbon monoxide, and several others in smaller numbers. A substantial number of the instruments are operated by large users (defined as possessing five or more instruments). Users remarked on the performance of the instruments. We noted these remarks as a measure of their satisfaction but we did not investigate the validity of the comments.

Table 8 lists manual methods used by the PHS Air Quality and Emission Data Branch (formerly the Air Quality Section).

Table 9 summarizes manual methods in use for ambient air analysis. Arranged in order of decreasing number of samples per year, the pollutants are: sulfur dioxide; fluorides, including hydrogen fluoride; suspended particulates, including various analyses of components; nitrogen oxides: oxidants; aldehydes; dustfall; carbon monoxide; and various others in smaller numbers.

First collaborative study

In March 1967 the Analytical Methods Evaluation Service announced its first collaborative study by direct mailing to all those laboratories which had registered, to members of the Intersociety Committee and its subcommittees, to appropriate committee members of the participating organizations, and to various others. About 90 laboratories indicated their interest in participating. Each was then sent a pair of sulfur dioxide permeation tubes, with instructions.

The primary objective of this collaborative study is to evaluate the permeation tube technique as a primary standard method for generating calibration concentrations of sulfur dioxide in air. Evaluation is based on a study of the accuracy and the reproducibility with which such tubes can be utilized.

A secondary objective is to obtain data that indicate the accuracy and the precision with which some of the presently used analytical methods can determine known concentrations of sulfur dioxide. Retrospectively, these data will permit an estimate of the accuracy of data originally obtained by any method. More detailed evaluations of analytical methods, including effects of interfering substances, may be made in future studies.

A third objective is to develop and refine one or more preferred techniques by which the constant flow of sulfur dioxide from a permeation tube may be diluted to a desired concentration under field or laboratory conditions.

O'Keeffe and Ortman (1966) showed that a liquefiable gas such as sulfur dioxide, when enclosed in an inert plastic tube, escapes by permeating the tubing wall at a constant, reproducible, temperature-dependent rate. They suggested the use of such tubes as primary standards for chemical or instrumental analyses of air pollutants. The plastic tubes were calibrated gravimetrically, the weight loss of a tube being assumed to be the weight of escaped gas.

Scaringelli, Frey, and Saltzman (1966) demonstrated exact equivalence between weight loss and sulfur dioxide effusion by measuring the latter both colorimetrically and microcoulometrically. Thomas and Amtower (1966) also reported successful tests.

Procedure used

Each collaborating laboratory will set up a flow system of its own choice. Certain specifications are given, the most important of which is controlling temperature to $\pm 0.1°$ C., preferably within the range 20–30° C. This is necessary because of the high temperature coefficient of the permeation rate.

The temperature coefficient is high principally because the permeation process requires that the molecules of sulfur dioxide have a certain minimum activation energy temporarily to rupture the weak bonds connecting the polymer chains in the tubing as they

Table 5
Continuous monitoring instruments in use for nitrogen oxides in ambient air[a]

Type	Number of labs possessing instrument	Number of instruments	Remarks by laboratories on performance[b]
Colorimetric:			
Beckman Instruments, Inc.	13	32[c]	(1,1,1,1,1) no comment; (12,6,1) good; (1) fair; (3[c]) continued maintenance and periodic calibration required; (2) poor; (1) trouble with calibration, readings with NaNO₂ are one half what they should be; (1) terrible
Borman[e]	2	13[c]	(11) good; (2[c]) continued maintenance and periodic calibration required
Harold Kruger Instruments[e]	1	3[c]	(3) continued maintenance and periodic calibration required
Precision Scientific Development Co.	2	3	(2,1) no comment
Kimoto Electric Co. (Japan)	1	1[c]	(1[c]) no comment
Homemade	1	3	(3) excellent but large
Any type	18[d]	55[c]	

Methods of standardization:
Generally dynamic with NO₂ gas, **vs.** Saltzman manual method; also NaNO₂ solutions.

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[a] Reports received before April 25, 1967.
[b] Number of instruments of this type possessed by the laboratory making this comment is indicated in ( ). Thus, (10,3) denotes that this remark was made by two laboratories, having 10 and 3 instruments, respectively. Validity of the comments was not investigated.
[c] Number estimated; some laboratories did not exactly specify numbers and types.
[d] This number is less than the sum of the preceding items because some laboratories have more than one type of instrument.
[e] No longer manufactured.

Table 6
Continuous monitoring instruments in use for carbon monoxide in ambient air[a]

Type	Number of labs possessing instrument	Number of instruments	Remarks by laboratories on performance[b]
Nondispersive IR:			
Mine Safety Appliances Co.	4	27[c]	(5) excellent; (1) excellent but large; (10[c]) good; (11) satisfactory
Beckman Instruments, Inc.	9	17[c]	(2,1[c],1) no comment; (1) very good with SiO₂ dryer; (1[c],1,1) good; (2) generally not too good, expensive to replace parts; (7) Monobeam—no longer manufactured
Unspecified or home-made	2	5	(1) excellent; (4) good
Any type	14[d]	49	

Method of standardization:

Generally standard CO mixtures in cylinders.

---
[a] Reports received before April 25, 1967.
[b] Number of instruments of this type possessed by the laboratory making this comment is indicated in ( ). Thus, (10,3) denotes that this remark was made by two laboratories, having 10 and 3 instruments, respectively. Validity of the comments was not investigated.
[c] Number estimated; some laboratories did not exactly specify numbers and types.
[d] This number is less than the sum of the preceding items because some laboratories have more than one type of instrument.

Bernard E. Saltzman *is Research Professor of Environmental Health at the Department of Environmental Health, College of Medicine, University of Cincinnati, a position he has held since October 1967, when he retired with the grade of Sanitary Engineer Director from the U.S. Public Health Service. Dr. Saltzman joined the PHS in 1941 as a sanitary engineer in Massachusetts and New York State. From 1943–44 he was a stream pollution chemist in Charleston, W. Va., and from 1945–60, an occupational health chemist in Cincinnati, Ohio. In 1960 he was appointed chief of laboratory in the Occupational Health Field Station, Salt Lake City, Utah, and in 1962 he was named deputy chief, Chemical Research and Development Section, Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Cincinnati, Ohio. In this capacity Dr. Saltzman wrote the accompanying article.*

Dr. Saltzman received his B.Ch.E. (1939) from the College of the City of New York, his M.S. (1940) in chemical engineering from the University of Michigan, and his Ph.D. (1958) in chemical engineering from the University of Cincinnati. A prolific writer and the holder of several patents, Dr. Saltzman is a member of ACS, the American Industrial Hygiene Association, the American Conference of Governmental Industrial Hygienists, the Air Pollution Control Association, the Association of Official Analytical Chemists, and the American Society for Testing and Materials.

Table 7
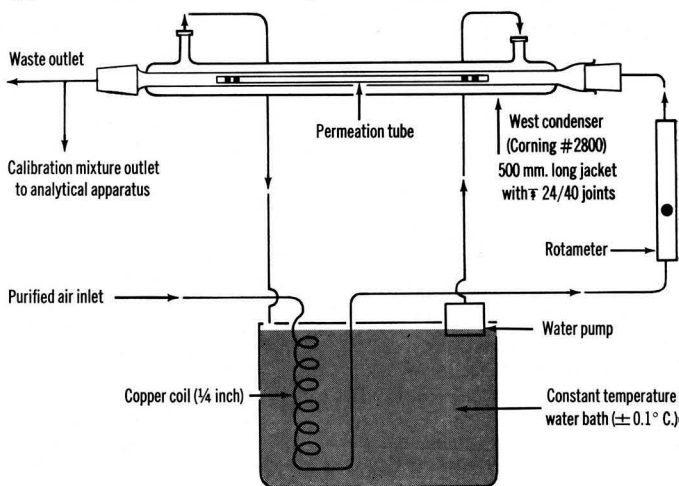### Miscellaneous continuous monitoring instruments in use for ambient air[a]

Type	Number of labs possessing instrument	Number of instruments	Remarks by laboratories on performance[b]
Tape samplers:			
American Iron and Steel Institute—Research Appliance Co.	14	64[c]	(20,1[c],1[c],1,1,1) no comment; (6) excellent after valve replacement; (12,5,1) good; (7) fair to good; (4,3) satisfactory; (1) photocell has short life;—(20,7,5,4,1,1,1,1,1) used for H_2S
Gelman Instrument Co.	2	3	(2) satisfactory with modified flow regulation; (1) sampling inconsistent
Mine Safety Appliances Co.	1	1	(1) motor problems, short life
Km–custom (Chaney)	1	12	(12) good
Any type	18	80[c]	
CO_2—Nondispersive IR:			
Beckman Instruments, Inc.	1	2	(2) no comment
Mine Safety Appliances Co. Model 200	1	1	(1) fair
Miscellaneous:			
Barton—reducing sulfur gases	1	1	(1) satisfactory
Homemade—mercaptans	1	1	(1) good
Instrument Development Co., 914 series—fluoride	1	1	(1) no comment
Mine Safety Appliances Co. Billionaire—acids and bases	1	1	(1) poor
Nuclear Measurements Corp.—particulate radioactivity	1	1	(1) good

[a] Reports received before April 25, 1967.
[b] Number of instruments of this type possessed by the laboratory making this comment is indicated in ( ). Thus (10,3) denotes that this remark was made by two laboratories, having 10 and 3 instruments, respectively. Validity of the comments was not investigated.
[c] Number may be greater; only one instrument of each type was credited to some laboratories not indicating number.

Apparatus with constant-temperature bath

Waste outlet

Permeation tube

West condenser (Corning #2800) 500 mm. long jacket with $\mp$ 24/40 joints

Calibration mixture outlet to analytical apparatus

Rotameter

Purified air inlet

Water pump

Copper coil (¼ inch)

Constant temperature water bath ($\pm$ 0.1° C.)

Figure 1

Apparatus with constant boiling liquid

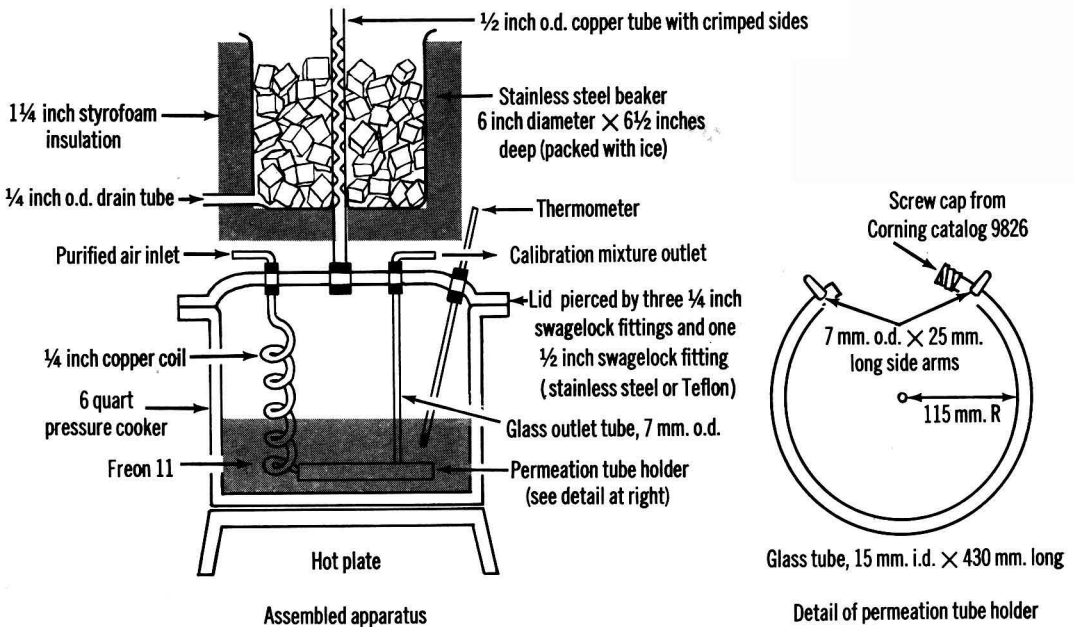Assembled apparatus

Detail of permeation tube holder

Figure 2

pass through in a series of discontinuous jumps. The energy released when the bonds recombine behind the molecules is not available for the permeation processes. Added to this activation energy is the requirement for heat of vaporization of the sulfur dioxide; this requirement is reflected in the change in vapor pressure with temperature. The vapor pressure provides the driving force for the permeation process.

Figures 1, 2, and 3 illustrate some systems for using the permeation tubes. The Figure 1 system is most convenient for a laboratory. In certain cities tap water may be used as a substitute for a thermostated water bath when the temperature from the mains is sufficiently constant for several hours. Figure 2 illustrates a system using Freon 11 ($CFCl_3$) as a safe reflux liquid with a convenient boiling point (23.5° C.); Freon 11 is available from refrigeration supply houses. For calibration of instruments where facilities are very

Table 8
Manual methods applied for National Air Surveillance Networks[a]
by Laboratory Services Activity

Pollutant	Sampling period (hours)	Method	Samples per year
Suspended particulates	24	Hi-vol. sampler-gravimetric	5950
		Hi-vol. sampler, sulfate (methyl thymol blue)[b]	5000
		Hi-vol. sampler, nitrate (hydrazine reduction-diazo coupling)[b]	5000
		Hi-vol. sampler, NH_3 (Nessler)[b]	5000
		Hi-vol. sampler, arsenic (silver diethyldithiocarbamate)	7000
		Hi-vol. sampler, metals (emission and atomic absorption spectrography)	1000
	24[c]	Hi-vol. sampler, benzene soluble (gravimetric)	1100
	24[c]	Hi-vol. sampler, benzo[a]pyrene (TLC-fluorescent)	500
SO₂	24	West-Gaeke[b]	1300
NO₂	24	Jacobs-Hochheiser[b]	1300
NH₃	24	Nessler[b]	1300
Sulfation	720	Lead candle-methyl thymol blue[b]	400
Aldehyde	24	MBTH	300
H₂S	24	Methylene blue	50

[a] Formerly known as National Air Sampling Network, PHS.
[b] Automated.
[c] Quarterly composite of samples.

Table 9
Manual methods in use for ambient air analysis[a]

Pollutant	Sampling period (hours)	Method[b]	Number of labs using method	Samples per year	Large users[c] Number of labs	Large users[c] Samples per year
SO₂	720	Lead candle	10	3,530	3	2,000
	72	H₂O₂-NaOH titration	1	4,500	1	4,500
	24	West-Gaeke	8	1,676		
	6	West-Gaeke	1	6,000	1	6,000
	4 or less	West-Gaeke	27	29,480	11	27,650
		Any method	39[d]	45,186	15[d]	40,150
F, HF	720	Lime filter-ECR	2	220		
	12 to 24	Thorium nitrate titration	1	2,000	1	2,000
	8	SPADNS-colorimetric	1	780	1	780
	6	Willard-Winters	1	6,000	1	6,000
	4	Technicon	1	4,500	1	4,500
	3	SPADNS-colorimetric	1	12		
	2 to 4	Colorimetric	1	1,000	1	1,000
	Variable	Conductivity	1	2,000	1	2,000
	Short	Neutral KI	1	?[e]		
	Short	USBM-RI 6314	1	180		
		Any method	11	16,792[e]	6	16,280
Suspended particulates	24	Hi-vol. sampler, gravimetric	8	9,500[e]	6	9,500
		Hi-vol. sampler, sulfate (turbidimetric)	5	4,200[e]	2	4,000
		Hi-vol. sampler, nitrate	3	4,300	2	4,000
		Hi-vol. sampler, benzene soluble	2	400		
		Hi-vol. sampler, polycyclics (UV + fluorescence)	1	2,000	1	2,000
		Hi-vol. sampler, metals (spectrographic, atomic abs.)	3	1,200	2	1,100
		Hi-vol. sampler, lead (polarographic)	1	2,000	1	2,000
		Hi-vol. sampler, iron (tripyridine)	1	?[e]		
	1	Millipore filter; arsenic (silver diethyldithiocarbamate)	1	1,000	1	1,000
	1	Millipore filter, microscopic	1	50		
	24	Ragweed pollen (microscopic)	1	180		
		Any method	9	12,680[e,f]	7[d]	12,200[e,f]
NO, NO₂	24	Jacobs-Hochheiser	3	1,100	1	500
	½ or less	Jacobs-Hochheiser	1	100		
	24	Saltzman	3	516		
	2 or less	Saltzman	23	6,528[e]	6	4,600
	2 or less	Mueller-Lodge (NO)	1	200		
		Any method	29[d]	8,444[e]	6	5,100
O₃, oxidant	360	Rubber strips-cracking	1	?[e]		
	168	Rubber strips-cracking	1	500	1	500
	24	Alkaline KI	1	?[e]		
	1 to 2	Alkaline KI	2	120		
	1 to 2	Unstated	1	200		
	3 to 6	Na diphenylamine sulfonate	1	50		
	½ or less	Neutral KI	13	1,728[e]		
	½ or less	Phenolphthalin	3	1,950	1	1,500
	½ or less	Unstated	1	1,000	1	1,000
		Any method	23[d]	5,548[e]	3	3,000
Aldehyde	24	MBTH	1	100		
	1 or less	MBTH	4	2,200	2	2,000
	?	Bisulfite	3	210		
	½	Chromotropic acid	1	288		
		Any method	8[d]	2,798	2	2,000
Dustfall	720	PHS, miscellaneous	6	1,812	2	1,220
	24 or less	Acidity or alkalinity	1	50		
CO	½	MSA-NBS detector tube	4	1,180	1	1,000
H₂S	1 to 2	Methylene blue	4	410[e]		
RSH	1 to 2	Moore, Calif. State Dept. of Public Health	1	200		
H₂SO₄	2	Cummins	1	50		
Hydrocarbons (C₁-C₆)	1	Gas chromatography	1	75		
NH₃	1	Indophenol blue	1	200		
	1	Nessler	1	75		
Pyridines	2	Silicate column–cyanogen bromide	1	100		

[a] Reports received before April 25, 1967 (excluding National Air Sampling Network).
[b] Including modified forms.
[c] At least 500 samples per year for listed method.
[d] This number is less than the sum of the preceding items because some laboratories use more than one method for a given pollutant.
[e] Actual number is greater because a few laboratories did not list the number of samples per year.
[f] This number is less than the sum of the preceding items because of multiple analyses of some samples.

limited, a heat sink, as illustrated in Figure 3, may be employed.

Tube construction

Figure 4 illustrates the construction of the permeation tubes, which are manufactured from $\frac{3}{16}$-inch i.d. FEP Teflon tubing with 0.030-inch wall thickness. Stainless steel balls of $\frac{7}{32}$-inch diameter are used to seal the liquid sulfur dioxide in lengths of 10 and 30 cm.

Each laboratory will analyze mixtures of sulfur dioxide in air in the range of 0–2 p.p.m. by the method or instrument of its own choice. The permeation rates, in micrograms of sulfur dioxide per minute per centimeter of tube length, will be computed and corrected to 25° C. by means of the chart in Figure 5. This chart is applicable only for the particular tubing used in this study.

Each laboratory was supplied with forms for a preliminary report to be sent within three months after receipt of the tubes and for reports on later measurements to determine the consistency of output of the tubes over at least a three-month period.

We believe that the technique is simple, convenient, and relatively inexpensive. It will be especially useful for calibration of instruments and for future studies of any particular analytical method. The tubes, which probably have a useful lifetime of one year, may be retained by the laboratories after the work is completed. Results of the study will be made available to the participants and to the Intersociety Committee and will also be published.

Further improvements

Selection of standard methods need
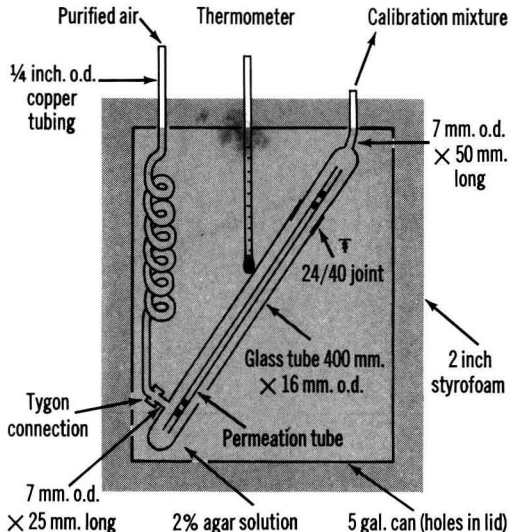
Apparatus with a heat sink

Figure 3

not retard either progress in research or the development of new methods. A standard method is not necessarily the best method. Rather, it is one the approving group has tested and found to be valid within a certain degree of error. Such a method provides the basis for certain legal activities. It also may be used as a reference for comparison with improved methods. Laboratories should be encouraged to use any improved new method if they can demonstrate satisfactory agreement with the standard or reference procedure or can clearly show a hitherto unrecognized weakness of the reference procedure.

The testing of methods requires the broadest possible participation. Scientific talent is needed from all levels of government, professional organizations, industrial laboratories, and educational and research institutes. The widest variety of approaches and experiments should be sought.

Any program of laboratory testing must include publication of the results. The participants should be listed for two reasons: to fix general responsibility, and to provide recognition, even if the standard methods based upon this work are ultimately issued by the sponsoring organization in an anony-
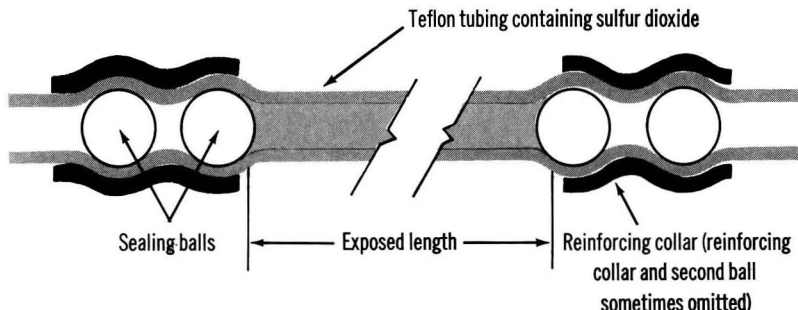
Construction of sulfur dioxide permeation tubes

Figure 4

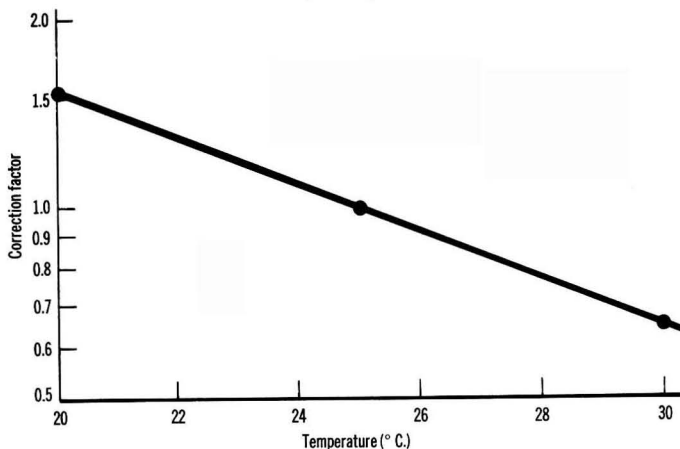**Correction of observed permeation rate to standard temperature (25° C.)**

Figure 5

mous manner. However, the results of individual participants should remain anonymous.

A good start has been made in standardization activities. Participation will aid groups engaged in pollution measurements to keep up with the latest developments and to compare their results with those of others. Adequate progress will require proper recognition and emphasis of this work. Qualified individuals should be allowed generous, though reasonable, use of official time and facilities, as well as of travel funds, to participate in committee activities. Research support should be provided.

Finally, during program planning, appropriate funding should be arranged. Probably 5 to 10% of the budget of a laboratory engaged in measuring pollutants should be allocated for participation in standardization activities. Only if we proceed in this broad manner can we progress at the rate needed to provide effective tests to implement adequate control and management programs.

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Fate of Airborne Benzo[a]pyrene

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■ Little is known of the fate of arenes in the atmosphere. To gain some knowledge of behavior of these arenes, benzo[a]pyrene in solid phase was studied under various treatments. Infrared analyses were used to describe the changes which occurred under treatment (900 to 700 cm.$^{-1}$ out-of-plane C—H bending vibration). Other isomers of B(a)P, perylene and B(e)P, and a few other polynuclear aromatic hydrocarbons did not show any changes in infrared curves under the same treatments. Hypothetical structural analyses also were postulated regarding the soot and polynuclear aromatic hydrocarbons, as polynuclear aromatic hydrocarbons do not exist when there is no soot.

Incomplete combustion is well accepted as the primary source of airborne benzo[a]pyrene, B(a)P. In contrast, little is known of its ultimate fate in the atmosphere other than it does disappear only to be continuously replaced (Green and Lane, 1964). This paper presents a number of related observations which give some insight into the fate of airborne B(a)P. Three major areas discussed are the state or phase of the airborne B(a)P; factors relating it to its carrier, soot; and its photochemical modification in the airborne state. Although emphasis is being placed on B(a)P, comparable conclusions can be drawn for many other polynuclear hydrocarbons.

Airborne Phase of Benzo(a)Pyrene

Commins (1962) concluded that no measurable amount of fluorescent hydrocarbons exists as vapors in the air at atmospheric temperatures because there was no detectable appearance of fluorescence after filtered air was drawn through pure liquid paraffin for 38 days. As B(a)P fluoresces, it may be inferred that it is not present in gaseous form.

The authors attempted to verify this using a combustion system (Mukai et al., 1964) as an effluent source which incorporates a recovery train for quantitative recoveries. The total combustion effluent was filtered through a tared glass thimble maintained at 80° to 90° C. to prevent moisture condensation. An aqueous phase was then condensed from the stream, followed by a dry ice–acetone condensate. A dead-end system collected all fixed gases. The amount of B(a)P contained in the condensates and fixed gases was used as an index of the amount that might be found in the gas phase.

The results of a typical combustion run indicate that a small percentage can be found in the gas phase at somewhat elevated temperatures close to the combustion source (Table I). Sublimation from the particulate trap was ruled out as the source of the small amount of the gaseous B(a)P by drawing air through a heated trap containing soot for a period corresponding to the combustion run. No B(a)P could be detected in the condensates from this air stream, which is consistent with no detectable recovery from a conventional sublimation coldfinger using pure B(a)P at 100° C. at atmospheric pressure within a period of one hour. (Sublimation is detected at temperatures slightly below 200° C.) The weight of B(a)P contained on deposited soot from the upper portion of the glass chimney of the furnace per unit weight of deposited soot was the same as the weight of the B(a)P per unit weight of filtered

Table I. Typical Combustion Run

Run	June 10, 1966
Fuel	Propane 492 cc. per minute
Primary air	None
Secondary air	5.7 liters per minute
Duration of run	70 minutes
Total soot	958 mg.
Total B(a)P	1800 μg.
On filter	1731 μg.
In H₂O trap[a]	54 μg.
In cold trap[a]	15 μg.
Isopropyl alcohol	40° C.
Fixed gas phase[a]	None

[a] % vapor phase $\frac{54 \text{ μg.} + 15 \text{ μg.} \times 100}{1800 \text{ μg.}} = 3.7\%$.

soot, indicating that the adsorption of B(a)P to the soot occurred prior to the filter and not as it was being drawn through the filtered soot. Therefore, all measurable quantities of airborne B(a)P are associated with airborne soot, the quantity in the gas phase being insignificantly small.

Bonding of B(a)P to Soot

There are numerous types of soot, with each particular soot having unique properties. The relationship between the various types of soot and carbon in general is given in Table II. Compilations of the physical and chemical properties of industrial soot have been prepared (Smith, 1964), but unfortunately information about airborne soot is meager. The major differences between industrial soot and airborne soot result from the mode of formation. Industrial soots are all quenched in the process of manufacture to maximize soot production, with the type of quenching and fuel imparting characteristics such as particle size, surface activity, and chain structure which are important in commercial usage. In contrast, conventional combustion processes, which are primarily responsible for airborne soots, generally minimize quenching to maximize thermal yields. Industrial soots are generally of a small diameter, with minimal chain structure, and are relatively "clean." Airborne soot particles are generally of a large diameter, have considerable chain structure, generally incorporate relatively large concentrations of benzene-extractables, and have a high volatile component. (Volatile component equals the per cent weight loss at 927° C. on a dry basis.) For example, furnace oil blacks, the "dirtiest" comparable commercial soots, run about 1% volatile component with a benzene extract of 0.05%, while airborne soots run about 20% volatile component with a benzene extract of 0.5 to 1% (Smith, 1964).

Airborne soots continue to agglomerate in the atmosphere until deposition and fallout occur. The authors are currently studying coagulation and deposition of airborne soot. The study considers such factors as the net charge and dipole on airborne soot particles, how these change with time, and how they are affected by light, temperature, electrical fields, and mechanical turbulence. Needless to say, the properties of airborne soot change with time.

Benzo[a]pyrene belongs to the arene class of hydrocarbons—i.e., it is a condensed polynuclear aromatic hydrocarbon, and all but one of the benzene rings is pericondensed. Soot may be thought of as an agglomerate of pericondensed polynuclear aromatic hydrocarbons. X-ray diffraction has definitely established that soot particles exhibit the hexagonal symmetry of graphite crystals (Houska and Warren, 1954; Warren, 1941). Numerous well-developed graphitic platelets, having a carbon skeleton analogous to a large polynuclear aromatic molecule consisting of 50 to 100 pericondensed rings, comprise the layer planes in a soot particle. The platelets in adjoining planes are stacked roughly parallel to one another but random in orientation. Several loosely bound adjacent platelets comprise a crystallite, and several thousand interconnected crystallites constitute the individual soot particle. During soot formation, oxidation occurs generally on the surface, resulting in the incorporation of 5 to 10% oxygen covering 30% of the surface area in addition to the 1 to 3% hydrogen also associated with the average soot particle (Riven, 1963; Rossman and Smith, 1943). The chemical structure of the surface groups identified on carbon

Table II. Relationship between Various Types of Soot and Carbon in General

| Noncolloidal Carbon[a,b]	Colloidal Carbon or Soot[c,d,e]
A. Diamond	A. Industrial soot or carbon black
B. Graphite carbon	
1. Graphite *per se*	1. Lamp black
2. Vitreous or retort carbon	2. Channel black
	3. Furnace black
3. Amorphous carbon (charcoal, coke)	4. Acetylene black
	5. Thermal black
4. Coal (qualified)	B. Airborne soot
5. Activated carbon	X. (Activated carbon)

[a] All of crystalline structure except coal.
[b] All naturally occurring except coke and charcoal (and activated carbon).
[c] All of crystalline structure based on x-ray diffraction (referred to as "amorphous carbon" based on microscopy).
[d] All synthetically produced during combustion except thermal black which is produced pyrolytically.
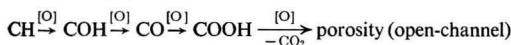[e] Only channel blacks and activated carbon exhibit open-channel porosity.

Figure 1. Soot particle
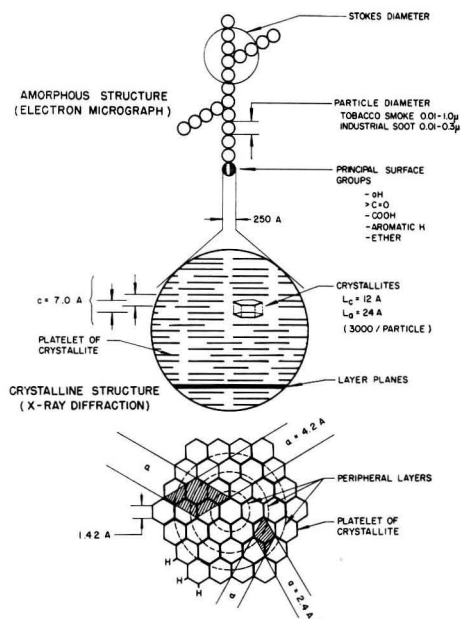
Peripheral Layers		Total Rings	Total Carbon	Total Hydrogen
Benzene =	0	1	6	6
Coronene =	1	7	24	12
	2	19	54	18
	3	37	96	24
	4	61	150	30
	5	91	216	36

Graphite c = 6.7 A.
        a = 2.4 A.
        a = 4.25 A.

blacks suggests that oxidation occurs predominantly in a stepwise manner.

$$CH \xrightarrow{[O]} COH \xrightarrow{[O]} CO \xrightarrow{[O]} COOH \xrightarrow[-CO_2]{[O]} \text{porosity (open-channel)}$$

This explains the process of forming activated carbon: Various forms of carbon blacks or charcoal are heated in an oxygen atmosphere to increase their open-channel porosity. Of all the soots, only acetylene blacks and small-diameter channel blacks exhibit appreciable open-channel porosity as verified by helium displacement (Rossman and Smith, 1943).

A hypothetical diagram of a soot particle consistent with x-ray diffraction data is presented in Figure 1. It assumes that each platelet is a symmetrical peripheral extension of coronene. An extension of three additional peripheral benzene layers results in a $C_{150}H_{20}$ molecule of 61 fused rings; four additional layers result in a $C_{216}H_{36}$ molecule of 91 fused rings. Both compounds have approximately the same percentage of hydrogen associated with them as is given by the chemical analysis of extracted soot. Calculation of the number of $C_{216}H_{36}$ molecules (ca. 3200) or the number of $C_{150}H_{30}$ molecules (ca. 4800) that can be placed consistent with crystallographic data in the volume of a hypothetical soot particle of a diameter of 250 A., results in an estimated density of 1.76 and 1.78 grams per cc., respectively. This corresponds to a figure of 1.8 grams per cc. employed by the rubber industry for industrial soots (Smith, 1964) and 1.90 grams per cc. determined by helium displacement (Rossman and Smith, 1943).

The lack of open-channel porosity, the large concentration of oxygen functional groups on the surface of the soot particle, and the adherence of airborne B(a)P to the particle in a manner that allows for ready extraction indicate that the B(a)P and other arenes are primarily adsorbed on the surface of the soot through hydrogen bonding. Chemisorption is not too feasible, because the rapid rate of photomodification indicates that B(a)P must be primarily in an exposed position on the surface. If the bonding is stronger to some functional groups than others, an explanation of the phenomenon of graded elution from soot particles is offered.

Relationships in Relative Yields of B(a)P and Soot

Yields of soot and benzene-extractables for several fuels burned under comparable conditions of incomplete combustion are compared in Table III. The yield of B(a)P is proportional to the weight of benzene extract (Mukai et al., 1964, 1965; Thomas et al., 1957). The relative proportion of B(a)P to the other arenes in each extract is also constant (Mukai et al., 1964, 1965; Thomas et al., 1957). Analysis of sized fractions using a Goetz aerosol spectrometer prior to extraction indicated that the amount of B(a)P per unit weight of soot was constant for all particles (Tebbens et al., 1966). The relative yield of soot per gram of fuel can be predicted from established smoking tendencies of fuels, which in turn can be related to fuel structure (Gaydon and Wolfhard, 1960). However, it is very difficult to make predictions on the yield of B(a)P based on fuel structure. For example, methane and acetylene produce equal amounts of extractable material, whereas acetylene produces almost eight times as much soot per unit weight of fuel; benzene, which has the same carbon-hydrogen ratio as acetylene, produces 12 times as much soot and benzene-extractables.
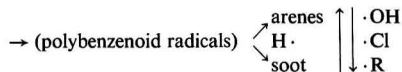
A possible insight might be gained from a comparison of proposed mechanisms of formation of soot and B(a)P. Several comprehensive reviews of carbon formation in flames are available (Gaydon and Wolfhard, 1960; Minkoff and Tipper, 1962; Parker and Wolfhard, 1950; Thomas, 1952), and a number of papers deal with the mechanism of B(a)P formation during pyrolysis (Badger et al., 1961, 1962a,b, 1963a,b; Gordon, 1948; Kinney and Crowley, 1954). It is difficult to

Table III. Yields of Soot and Benzene-Extractables Produced during Incomplete Combustion

Fuel	Mg. Soot/G. Fuel	Mg. Extractable/ G. Fuel	Mg. Soot/ Mg. Extractable	γB(a)P/Mg. Soot	Flow Rates
Methane	16	1.9	8.4		
1-Butene	72	9.4	7.7		
Acetylene	105	2.1	50.0		
Butadiene	135	14.4	9.4		
Benzene (gas)	196	21.3	9.2		

Burning conditions adjusted for maximum soot production. Fuel and air flow constant.

					Air, L./Min.
1-Butene	72	9.4	7.7		11 3
	56	1.4	40.0		25.1
	56	1.2	47.0		35.5
	49	1.2	41.0		47.0

Fuel flow constant.

					Fuel, Cc./Min.
Propane + H_2			1.81	5.28	41.5 + 5.1
			1.42	6.20	41.5 + 24.0

Propane and air flow constant.

relate pyrolysis information *per se* readily to pyrolysis occurring as part of the combustion process. Only steady-state flash pyrolysis approaches pyrolysis occurring during combustion. A rather naive hypothesis arrived at by a comparison of a number of mechanisms may be presented in equation form:

$$\rightarrow \text{(polybenzenoid radicals)} \begin{array}{c} \text{arenes} \uparrow \\ \text{H} \cdot \\ \text{soot} \downarrow \end{array} \begin{array}{c} \cdot \text{OH} \\ \cdot \text{Cl} \\ \downarrow \cdot \text{R} \end{array}$$

Polybenzenoid radicals may be produced through a variety of mechanisms. Continued polymerization of these radicals results in soot. Early termination of this final polymerization by hydrogen atoms results in enhanced arene production. The presence of high concentrates of any radical that will reduce the concentration of the hydrogen atom should favor soot; introducing hydrogen atoms from an external source (H_2 added to fuel) should favor arene production.

The hypothesis was roughly checked by comparison of the relative production of soot to weight of benzene-extractables (assuming the arene production is proportional to the benzene-extractable). Table III shows that when the air flow is increased (conceivably increasing $\cdot O$ or $\cdot OH$) using 1-butene as fuel, production of both soot and benzene extractables is decreased because combustion moves closer to stoichiometric conditions. However, the ratio of soot to extractables shows that the rate of extractable decrease is much more rapid than soot decrease. In another experiment when the hydrogen is added (Table III) in combination with propane, the reverse trend is shown, and there is an increase in benzene-extractable and in B(a)P. A reported instance of adding nitropropane to propane gas (a radical sink for $H \cdot$) is consistent with this: "Small additions of nitropropane lead to a marked reduction in the formation of pentane-soluble material in the soot and in the amount of 3,4-benzopyrene [now designated as B(a)P]. Rather surprisingly, the soot formation rises to a maximum with increasing amount of additive and then declines" (Long, 1962).

The following data suggest that a portion of the hydrogen may originate from the late pyrolysis of simple hydrocarbons formed during early pyrolysis. The flash pyrolysis of kraft black liquor is currently under investigation. The polyphenolic material comprising the liquor is injected at short intervals into a reactor vessel maintained at fixed temperatures, and the pyrolysis gases are directly chromatographed. A plot of methane and hydrogen production as a function of temperature is shown in Figure 2. The methane decreases and the hydrogen increases as the temperature increases. On a mole basis it is apparent that other gases, such as ethane and acetylene, must also contribute hydrogen during late pyrolysis. By quenching the combustion process, hydrogen production from late pyrolysis is minimized, and consistent with this hypothesis soot production should be maximized and arene production minimized. This is consistent with methods and findings in the production of industrial soots.

Photomodification of B(a)P

The photomodification of B(a)P has been studied previously, with the B(a)P being in crystalline form as a component of smoke from diesel engines caught on filter surfaces (Falk *et al.*, 1956), and in solution (Kuratsune and Hiro-
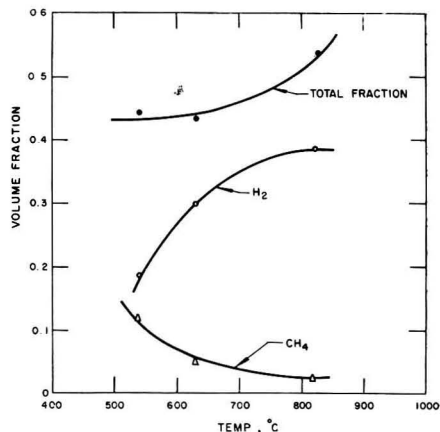
Figure 2. Pyrolysis of kraft black liquor at various temperatures

hata, 1962). The authors will attempt to extend basic concepts as well as to present information on the photomodification of B(a)P as contained on airborne soot (Tebbens *et al.*, 1966).

Airborne B(a)P on soot was studied by coupling a furnace (Mukai *et al.*, 1964) through a dilution chamber to a tubular reactor (~11 feet × 6 inches) (Tebbens *et al.*, 1966). Lighting is controlled up to one-quarter intensity of average July noonday sun. The soot particles are introduced as close to laminar flow as possible, with retention times determined by flow rates. The flow results from suction applied at the exit end. Flow characteristics are indicated in Figure 3. It is not feasible to reduce retention times in the reactor below one hour, because coagulation and sedimentation of the soot reduce the reliability of B(a)P analysis. Sampling is accomplished through tared glass thimbles at the entrance and exit ends of the reactor.

The amount of B(a)P per unit weight of soot at the exit end of the reactor and at the source end in both light and dark is compared in Table IV. A small decrease is noted in the dark but a very large decrease occurs very rapidly in the light. This further corroborates earlier observations (Tebbens *et al.*, 1966).

If one of the early hypotheses that B(a)P is primarily contained on the surface of soot is correct, one explanation for the

Table IV. Effect of Light on Production of Acid Fraction and Reduction of B(a)P

Sample	Flow Rate, L./Min.	Retention Time, Min.	Neutral, µg./Mg. Soot	B(a)P, µg./Mg. Soot	Acid, µg./Mg. Soot
Source	...	...	630.8	3.77	4.34
Light off	1.5	40	543.7	3.44	4.14
Light on	1.5	40	334.1	1.62[a]	28.44[b]

[a] B(a)P decrease 58%.
[b] Acid fraction increase 6-fold.

rapid disappearance is the very large exposed surface area on the colloidal-sized soot particles. To check the effect of surface area, a coating of 1 mg. of B(a)P was applied to 1 gram of glass beads of 220- and 28-micron diameters by evaporation from solution. The beads were placed in flasks exposed to the sun and agitated hourly to expose fresh surfaces. A visible yellow discoloration and a disappearance of fluorescence under ultraviolet light occurred in a matter of hours for the B(a)P contained on the small beads, whereas a corresponding change on the big beads took 5 to 10 days. Measuring the decrease of B(a)P by fluorescent techniques on ether extracts showed that approximately a 1% decrease had occurred in 12 hours on the small beads, but approximately 7 days in the sun was required for a corresponding decrease in the large beads. This compares to a 60% decrease in 40 minutes on the soot. Therefore, the relatively rapid decrease of B(a)P on soot may be related to much greater surface exposure to light.

Infrared spectroscopy was very sensitive as an indicator of these changes associated with the photomodification of B(a)P. (Unless noted, all infrared curves were obtained using the KBr pellet technique.) Jones and Sandorfy (1956) reported that all polynuclear aromatic compounds show intense absorption bands between 900 and 700 cm.$^{-1}$ characteristic of the out-of-plane C—H bending vibrations. A large number of arenes have been analyzed in detail in this region, and four subdivisions have been suggested based on the number of residual hydrogens on the peripheral benzene rings (Vingiello and Ojakoar, 1966). B(a)P shows spectral response in all four subdivision regimes: The hydrogens on the 1, 2, and 3 carbons are referred to as trio hydrogens and give a response in the 810- to 750-cm.$^{-1}$ region; 4, 5, and 11, 12 are duo hydrogens and give a spectral response between 860 and 800 cm.$^{-1}$;

6 is a mono hydrogen responding between 900 and 860 cm.$^{-1}$; and 7, 8, 9, and 10 are quartet hydrogens responding between 770 and 735 cm.$^{-1}$ Infrared curves for freshly chromatographed perylene, B(e)P, and B(a)P are shown in Figure 4, A, B, and C. Note the lack of solo response for B(e)P and the lack of solo, duo, and quartet response for perylene which are missing the corresponding hydrogens.

The infrared curve for B(a)P that has been exposed to light for several hours is modified compared to the freshly chromatographed B(a)P, as shown in Figure 4, D. Changes in intensity and frequency of the noted characteristic bands indicate changes in the carbon-hydrogen bending vibrations. A number of other similar hydrocarbons tested did not exhibit corresponding changes in their spectrum after exposure to light (anthracene, pyrene, benz[a]anthracene, benzo[e]pyrene, perylene, dibenz[a,h]anthracene, dibenzo[a,h]pyrene, and dibenzo[a,i]pyrene). Continued exposure to light causes no further changes in the infrared spectrum, other than an over-all decrease in intensity comparable to the decrease of fluorescent intensity related to the disappearance of B(a)P.

An ether extract of B(a)P coated on small beads after 12 hours of exposure showed a much stronger yellow color than the B(a)P on the large beads. Both the yellow of the small beads and the almost colorless large beads showed the modified infrared spectral changes. In both cases, however, it was difficult to demonstrate a reduction of B(a)P by fluorescent spectroscopy.

Chromatographing the yellow extract of the small beads through alumina using 20% ether in pentane results in three fractions. The eluted fraction contains pure B(a)P showing the original infrared spectrum of Figure 4, C. A yellow band halfway down the column indicated the presence of at least
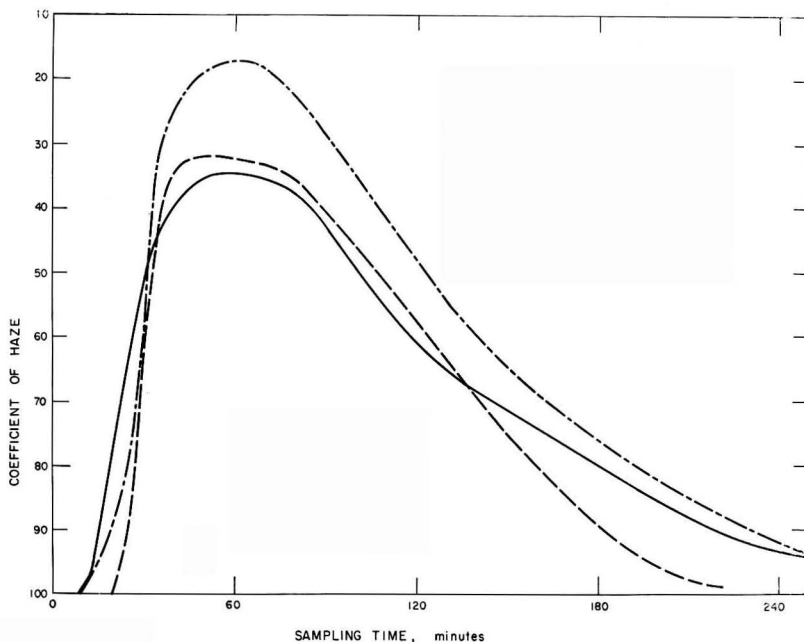
Figure 3. Flow characteristics of soot particles through reactor

two acidic components upon further treatment by paper chromatography. The undeveloped yellow fraction on top of the alumina column, probably of a very polar nature, likewise indicated the presence of several other acidic components. Adding these acidic components individually or combined back to the chromatographed pure B(a)P in only trace quantities also caused an infrared spectral modification. Subsequently, many compounds capable of hydrogen bonding were found to cause the modification. Excess dosing of known complexing agents—for example, picric acid or TNB—resulted in a hypsochromic shift of the entire spectrum, as shown in Figure 4, E.

When added in trace amounts to B(a)P, the majority of arenes used directly from the shelf caused the infrared modification. Upon chromatography of the arenes from the shelf, it was found that the pure arenes did not cause the modification but rather it was the residual chromatographed fraction, indicating the presence of oxygenated compounds. Heat as well as light and oxygenated compounds could also cause the infrared spectral modification.

All of the observations obtained using KBr pellets could be duplicated using a Nujol mulled technique or evaporating solutions of B(a)P directly on a rock salt window. Also, freshly crystallized B(a)P gives a curve comparable to freshly chromatographed B(a)P.

A consideration of reported information on the photochemical treatment of anthracene might offer an explanation of the infrared curves and modifications: "It was established that the changing of anthracene into dianthracene in the light was to be considered as a reversible photochemical reaction which goes to a stationary equilibrium condition" (Egloff, 1937).

Assuming that B(a)P might also be involved in a similar equilibrium, the following equation is presented in conjunction with spacial considerations of the C—H out-of-plane vibrations (Figure 5):

The following points are made relating to previously mentioned observations.

The undissociated B(a)P which gives the original spectrum shown on Figure 4, C, is very reactive, readily entering into equilibria involving complex formation.

The C—H out-of-plane vibrations may randomly occur on both sides of the B(a)P planar configuration, giving the original spectrum. Upon activation by light or heat a complex is formed, possibly a dimer, which locks the C—H out-of-plane vibrations to one side of the plane, resulting in the modified spectrum of Figure 4, D.

The complex thus formed may enter into further complex formation through hydrogen bonding to hetero atoms further locking the C—H out-of-plane vibrations, resulting in a

Figure 4. Infrared curves of B(a)P isomers

A. Perylene
  1. Solo   B. B(e)P
  2. Duo   C. B(a)P
  3. Trio   D. B(a)P + light
  4. Quartet E. B(a)P + complexing agent

A. EQUILIBRIUM CONSIDERATION
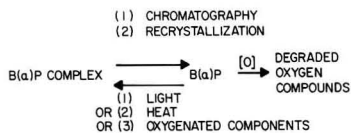
B. SPACIAL CONSIDERATION
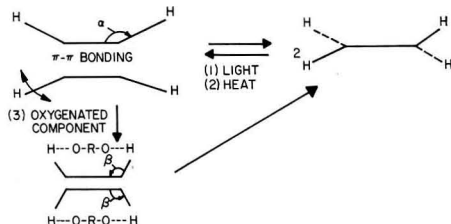
Figure 5. Hypothetical presentation of B(a)P complex formation as explanation for changes in infrared spectra

A. Equilibrium consideration
B. Spacial consideration

slight hypsochromic shift of the modified spectrum as shown in Figure 4, *E*.

In addition, the B(a)P readily undergoes oxidation with the products being hydrogen-bonded to the parent as indicated above.

Recrystallization or chromatography readily breaks complex formation, shifting the equilibrium back to the monomer form.

The infrared spectrum of an accumulation of the yellow material produced during irradiation of B(a)P is very complex, indicating a gross mixture, but there is a predominant carbonyl peak. The yellow material is readily extractable in dilute base and shows at least six fluorescent bands on paper chromatograms using a basic developer. The indication of acid groups is very obvious. Exposure of B(a)P to ozone, oxygen, or air results in the formation of yellow solutions in the light or dark. A greater variety of components at relatively high concentrations are produced in ozone and to a lesser extent in oxygen, indicating progressive degradations to simpler components depending on the availability of an oxidizing agent. However, exposure of B(a)P to sunlight in an inert atmosphere also results in the formation of similar products after an extended period. Possibly, trace amounts of oxygen are all that are required for the oxidation to occur.

Gas chromatographic techniques are being developed utilizing the new gas cell infrared detector. An array of possible products is currently being investigated based on information in the literature on chromic acid oxidation of B(a)P (Clar, 1964) and ozonalysis of B(a)P (Moriconi *et al.*, 1961); included are quinones, carboxylates, dicarboxylates, diacetates, anhydrides, and phenols.

A final interesting observation can be made concerning airborne B(a)P on soot, as indicated in Table IV. Comparing the decrease of B(a)P per unit weight of soot to the increase of acid fraction per unit weight of soot shows a manyfold increase of acid compared to the B(a)P decrease, probably due

to contributions of acids from other arenes. The possibility of the formation of the oxygenated B(a)P complex is greatly enhanced on the soot, thus reducing the relative concentration of the reactive B(a)P-monomer.

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Interaction of Nitrogen Dioxide–Olefin Gas Mixtures with Lecithin Monomolecular Films

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■ The interactions of nitrogen dioxide–olefin gas atmospheres with saturated and unsaturated lecithin monomolecular films were investigated using surface pressure measurements. Films of dipalmitoyl lecithin, a saturated phospholipide, showed no interaction with any of the test atmospheres used. Films of egg lecithin, an unsaturated phospholipide, showed significant changes in the surface pressure–surface area curves in the presence of all atmospheres containing nitrogen dioxide. The observed effects appear to be the result of a chemical interaction of NO₂ with the double bonds of the egg lecithin rather than a simple physical penetration of the film. Biological implications are discussed.

A number of methods, both biological and physical, have been used in an attempt to assess the cytological toxicity of air pollutants. Some of these methods have demonstrated that the observed toxic effects of certain pollutants are related, at least to some degree, to their ability to adsorb and act at the cell membrane. Mendenhall and Stokinger (1962) and Stokinger (1965) offered evidence that ozone exerts a direct effect upon the cell membrane. Reports that air pollutants inhibit plant cell wall metabolism and inhibit bacterial enzyme systems located in the cell membrane add further support to this idea that some pollutants may exert their in vivo effect via their ability to adsorb at cell membranes. While other factors, of course, must be involved, it seems reasonable to expect a relationship to exist between the toxicity of some air pollutants and their adsorption and interaction at cell membranes.

In the last decade, there has been a growing interest in the properties of cell membranes, their chemical make-up, and molecular orientation, particularly as related to their cellular activity. This has led to the isolation and characterization of membrane components from a wide variety of organisms, and the development of model systems utilizing these components. Particular emphasis has been directed toward the phospholipides (a group of compounds basic to membrane structure) because of their implication in a variety of biological processes.

Insoluble monomolecular films of phospholipides have been widely used to simulate the interactions at a molecular level of numerous materials with living membranes. The general usefulness of these films as cellular membrane models has been demonstrated by a number of researchers. Pethica and Schulman (1953) showed that the in vivo lytic action of a series of antibacterial agents was directly related to the ability of these compounds, when dissolved in the aqueous phase, to adsorb at a monomolecular lipide film. Skou (1958) developed a similar relationship for a series of anesthetic drugs. Since these early experiments, a number of workers have demonstrated similar relationships for a variety of drugs. More recently, Demel, van Deenen, *et al.* (1965) related the activity of polyene antibiotics to this same property. In addition, some of these studies showed that the interactions observed were due to the presence of a specific lipide, and in the absence of this lipide little or no interaction resulted either in vivo or in vitro. The work of Bondurant (1960), Clements and Wilson (1962), and Mendenhall and Stokinger (1962) extended the usefulness of spread-film models to include adsorption from the vapor phase. Bondurant (1960) reported the effect of cigarette smoke on the surface tension of lung tissue extracts. Mendenhall and Stokinger (1962) showed a marked change in surface pressure of films of lung extracts on exposure to ozone. Clements and Wilson (1962) employed a dynamic technique to determine the effect of a steady flowing stream of gaseous anesthetics on the surface tension of a film. Pure fatty acids and phospholipides, as well as lung extracts, were used as films in this latter study. A direct relationship

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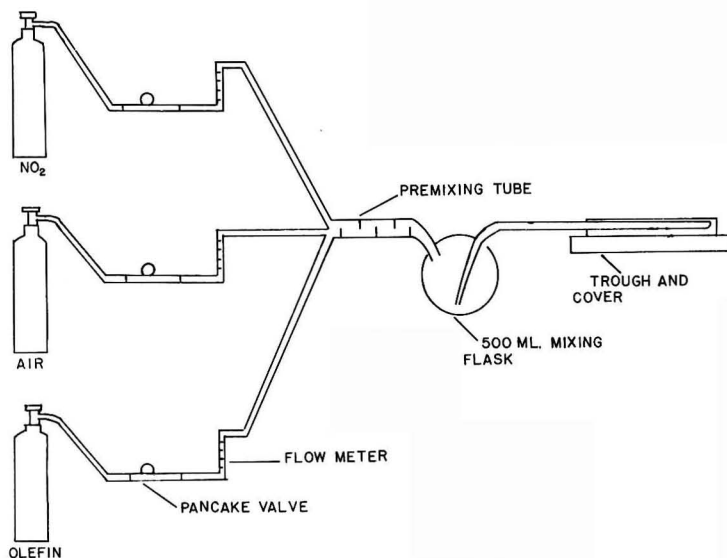
Figure 1. Schematic diagram of gas-mixing system

between anesthetic potency of a series of gaseous anesthetics and their ability to adsorb at a film was demonstrated by these workers. In addition, the observed biological changes in cellular permeability, excitability, and metabolic activity caused by these gaseous anesthetics could be explained by their ability to adsorb at cell membranes.

Dean, Hayes, *et al.* (1953) studied the effect of a number of gases, including nitrous oxide and ethylene, on monolayers of various fatty acids and phospholipides. The gases were found to cause only slight increases in surface pressure, which in no case exceeded 2 dynes per cm.

The purpose of this phase of the investigation is to compare the interaction of nitrogen dioxide-olefin gas mixtures with monomolecular films of dipalmitoyl lecithin (DPL) and egg lecithin (EL) to determine the influence of unsaturated fatty acid groups on this interaction.

Materials

Air, 1 % nitrogen dioxide in air, 0.25 % *trans*-2-butene in air, and 1 % ethylene in air were obtained either from the Matheson Co. (East Rutherford, N. J.) or J. T. Baker (Linden, N. J.). L-α-Dipalmitoyl lecithin (DPL) was obtained from Mann Laboratories (New York, N. Y.) and egg lecithin (EL) from Sylvana Corp. (Millburn, N. J.). The water used was prepared by fractional distillation of deionized water from basic permanganate using all-glass equipment. All other materials were reagent grade.

Apparatus and Methods

The gas mixtures were prepared by a procedure similar to that employed by Estes (1967). A schematic diagram of the system is shown in Figure 1. The gases were metered by individual flow meters into a glass tube equipped with baffles,

SIDE VIEW

TOP VIEW
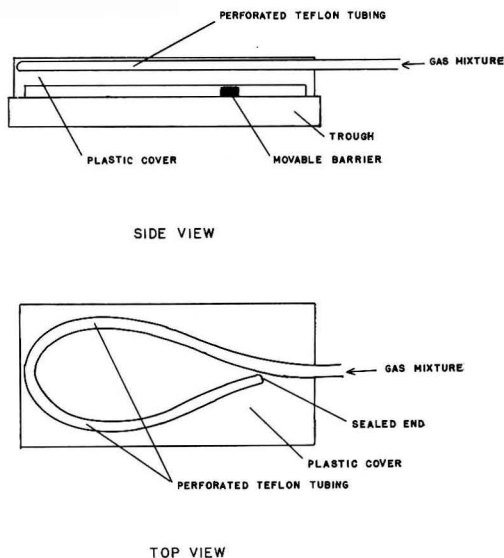
Figure 2. Schematic diagram of trough and cover unit used to spread and expose films

which served as a premixing tube. Mixing was completed by passing the gases into a 500-ml. round-bottomed flask. The gas mixtures were then led through a 3-foot length of glass tubing connected to a short length of Teflon tubing. The latter was affixed to the underside of the Lucite trough cover which served to maintain the desired gaseous atmosphere over the film (Figure 2). The Teflon tubing within this enclosure was formed into a loop, and a series of small perforations was made in the wall of the tubing. The shape of the loop and the positions of the perforations gave a uniform flow of the gases over the film surface.

The gas mixtures were permitted to flow through the system for at least four hours before the start of each experiment to ensure steady-state conditions.

A Film Balance (Frater Instrument Co., Corona, N. Y.) was used to study the surface pressure–surface area (π-A) characteristics of the films. The balance consists of a Teflon-coated removable trough, totally free of metal contacts. Two variable-speed reinforced rigid Teflon stirrers are set into the trough to facilitate subphase mixing and temperature control. The temperature of the subphase was maintained at $25° \pm 0.1°$ C. by circulating water from a constant temperature bath through the water jacket around the trough. The precision lead screw, which drives the reinforced Teflon barrier-allows for changes in surface area of the trough as small as 0.0125 sq. cm. A quick disengage mechanism permits rapid sweeping of the film for cleaning the surface. The film balance was enclosed in a dust protective cabinet.

Surface pressures were measured by the Wilhelmy plate method (Adamson, 1967). A thin platinum plate, roughened to ensure complete wetting, was used.

Solutions of DPL (0.5 mg. per ml.) in ethanol-hexane (5 to 95, v./v.) and EL (0.45 mg. per ml.) in ethanol-hexane (1 to 99, v./v.) were spread on 0.9% sodium chloride using an Agla micrometer syringe.

These films were studied while exposed to a standard atmosphere—i.e., air flowing at the rate of 300 ml. per minute or to the following test atmospheres, all flowing at this same rate of 300 ml. per minute: (a) 0.33% nitrogen dioxide in air; (b) 0.33% ethylene in air; (c) 0.08% trans-2-butene in air; (d) 0.33% each of nitrogen dioxide and ethylene in air; (e) 0.33% nitrogen dioxide and 0.08% trans-2-butene in air.

In all cases, the films were permitted to stand with the gases flowing for one hour before manual compression of the film was initiated. Surface pressure readings were then obtained at various film areas.

Results and Discussion

The π-A curve for DPL exposed to the standard atmosphere is shown in Figure 3. Exposure of DPL films to all of the test atmospheres yielded identical π-A curves—i.e., within ± 0.4 dynes per cm. at all areas. Thus, apparently neither the NO_2 nor the olefins interact with the DPL film.

Figure 4 shows the π-A curve for EL exposed to the stan-
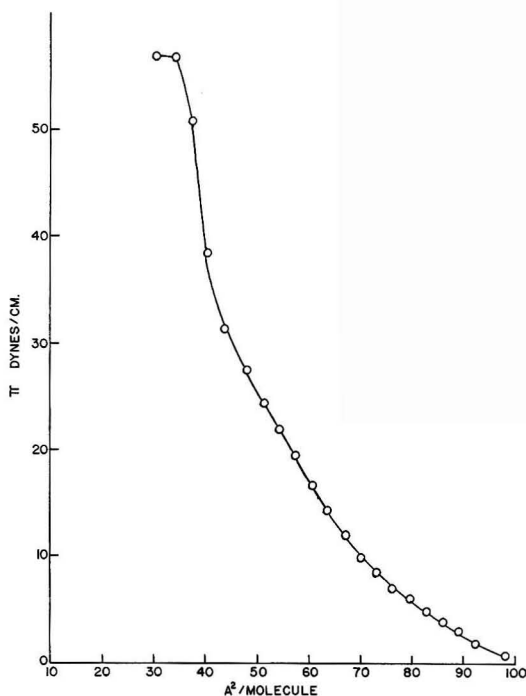
Figure 3. π-A curve of dipalmitoyl lecithin exposed to standard atmosphere (air) and all test atmospheres

dard atmosphere. Exposure of EL to test atmospheres b and c yielded curves that were identical to that obtained with the standard atmosphere. However, exposure of EL to test atmospheres a, d, and e resulted in π-A curves that were considerably more expanded than the standard EL curve. Thus, all the mixtures which contain NO_2 markedly affect the EL film. However, neither the ethylene nor the trans-2-butene exhibited any interaction with EL. The addition of the olefins to the NO_2 mixtures did not influence the EL-NO_2 interaction.

DPL and EL differ from one another only in their fatty acid composition. DPL contains only palmitic acid, a C_{16}, fully saturated fatty acid. EL contains both saturated and unsaturated fatty acids, mainly oleic and palmitic. Approximately 50% of the fatty acid groups of EL contain at least one unsaturated bond (Shah and Schulman, 1965). The observed interaction between NO_2 and EL films can, therefore, only be attributed to the presence of unsaturated bonds.

Interpretation of the data obtained in this study indicates that the resultant increase in area per molecule of the EL film in the presence of NO_2 involves a chemical reaction rather than a simple physical adsorption or penetration. First, if the effect was the result of simple penetration, the penetrant (NO_2) would probably be ejected from the film at high pressures. The π-A curves in both the presence and absence of NO_2 would then become identical at these high pressures. However, as can be seen in Figure 4, ejection was not observed;
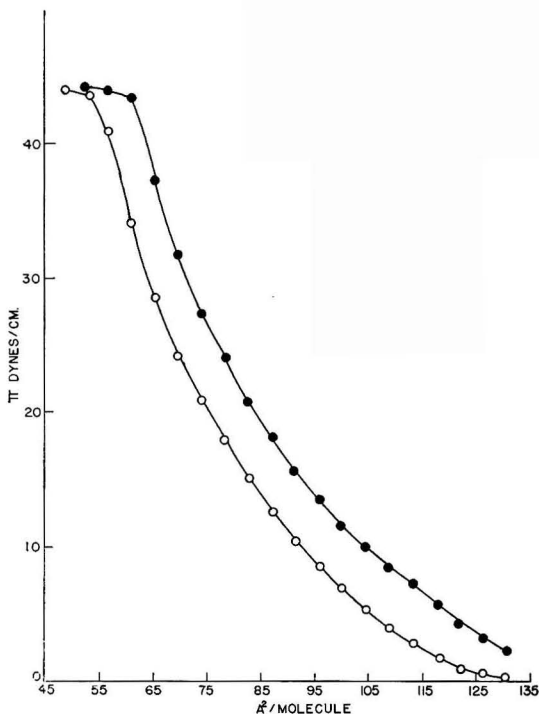
Figure 4. π-A curves of egg lecithin exposed to standard atmosphere (air) and test atmospheres *b* and *c* (○), and to test atmospheres *a*, *d*, and *e* (●)

instead the NO_2–EL film collapsed as a unit at an area per molecule of 62 sq. A. as compared with 52 sq. A. for the standard EL film. There have been some studies reported in which film penetration led to a sufficiently strong interaction for the film to collapse as a unit (Cockbain and Schulman, 1939). However, this occurs only when the penetrant molecule interacts strongly with both the polar and nonpolar groups of the film molecules. NO_2, a relatively small and extremely polar molecule, probably would not exhibit such properties. In addition, this type of penetration usually results in a collapse pressure much higher than is observed for the film alone. This latter effect also was not observed in our work.

Much more direct evidence indicating a chemical reaction was obtained in the following experiments. Separate EL films were exposed to each of the test atmospheres containing NO_2 (atmospheres *a*, *d*, and *e*). After exposure, the flow of gases was discontinued. The trough cover was then removed to allow rapid dissipation of the test atmospheres from the film surface. The cover was then replaced, and the standard atmosphere was allowed to flow over the film for one hour. This technique completely eliminated the test gases from the atmosphere above the film surface.

The π-A curves were still identical to that of Figure 4 (filled circles), indicating an irreversible interaction. Such an effect would not be expected if only simple physical adsorption or penetration was involved.

Pattle (1967) noted that lungs rendered atelectatic by exposure to various irritant air pollutants still showed evidence of functional lung surfactant. He also found that these irritants did not produce pulmonary collapse but rather pulmonary edema, apparently as a result of increased capillary permeability. These data imply that the primary site of attack of these irritants was not the lung surfactant, but rather the components of the capillary cell membranes responsible for membrane integrity.

The present work seems to support this postulation. Lung surfactant, which has been shown to be mainly dipalmitoyl lecithin (Klaus, Clements, *et al.*, 1961), is apparently resistant to NO_2. All cell membranes in general contain significant amounts of unsaturated phospholipides (Baer, 1966), and therefore would tend to interact with NO_2, resulting in an expansion and conceivably increased permeability.

While the authors recognize that this explanation is an oversimplification of an extremely complicated process, it may explain to some degree part of the mechanism of action of NO_2 on biological systems. Future work will be reported dealing with the interaction of pollutants with additional phospholipides and lipoproteins as well as the influence of irradiation of the pollutants on these interactions.

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Sulfur Hexafluoride as a Gas-Air Tracer

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■ Sulfur hexafluoride, a useful gas-air tracer, is separated in gas chromatography from other components of moist air on columns of silica gel and activated carbon in series, and is detected by electron-capture analysis in concentrations near 1 p.p.b. This sensitivity can be enhanced at least 2000-fold by freeze-out concentration. The maximum error in calculating the concentration of a diluted gas mixture is calculated on the basis of the fraction recovered in reconcentration. SF_6 backgrounds in air are undetectable except near leakage sources such as transformers. The use of SF_6 as a gas tracer to determine the dilution of a stack effluent gave results that were close to the calculated values.

H alogenated compounds have been shown to be suitable tracers for meteorological studies of moving air masses (Clemons and Altshuller, 1966; Collins, Bartlett, *et al.*, 1965; Saltzman, Coleman, *et al.*, 1966). SF_6 is particularly useful because it is amenable to ultrasensitive analysis by electron-capture detection, is convenient to handle and dispense into air, is odorless and nontoxic, is chemically and thermally stable, and does not usually occur in significant concentrations in outdoor air.

The present study describes a procedure for SF_6 analysis that is applicable to moist samples, a concentration procedure that enhances analytical sensitivity, a method of evaluating errors in dilution systems that is particularly relevant to problems of validating gas calibrations at very high dilutions, an examination of SF_6 atmospheric backgrounds, and an outdoor exercise in which SF_6 is used as a tracer of gas diffusion from a real stack.

Analytical Procedures

Sampling. A 1000-cu. inch stainless steel tank was provided with needle valves at both ends, a pressure gage at one end, and a constant differential-type flow controller at the other. The tank was evacuated in the laboratory, and was brought to the field for sampling. In comparative studies, the valve was opened in the field for a fixed time (usually 20 minutes) to permit control of the sample size. The partially evacuated tank was then brought back to the laboratory and pressurized with purified air to 45 p.s.i.g. Extreme precaution must be taken to avoid contamination of the sample with extraneous SF_6. In a laboratory where SF_6 is handled and may find its way into the air supply, the air used for pressurizing the tank should be filtered successively through Drierite, activated charcoal cooled with dry ice–acetone, and silica gel cooled with liquid oxygen. As an additional precaution, a partially evacuated tank must not be stored near a supply of SF_6.

Analysis. A Perkin-Elmer Model 810 gas chromatograph with electron-capture detector and ionization detector amplifier was used. Samples were introduced by connecting the pressurized sampling tank directly to the gas sampling valve and using the 5-ml. loop. The columns were 1-meter × 1/8-inch silica gel and 1-meter × 1/8-inch activated charcoal in series. Neither column alone would separate the sulfur hexafluoride from the three interfering substances in air: oxygen, carbon dioxide, and water vapor. The columns were maintained at 120° C. and the detector at 150° C. Prepurified nitrogen was passed through the system at a flow rate of 60 ml. per minute. Under these conditions, the sulfur hexafluoride emerged from the columns after 4 minutes, well separated from the interfering substances. A typical trace obtained from a 5-ml. gas sample is shown in Figure 1.

At the higher sensitivity settings of the ionization detector amplifier, electrical noise in the system was found to be excessive, and a filter consisting of a 3000-ohm resistor and a 10-μf. capacitor was placed between the output terminals of the ionization detector amplifier and the input terminals of the recorder. This decreased the noise to the point where the minimum detectable amount of sulfur hexafluoride was decreased by a full order of magnitude. More filtering was found to be undesirable, as it affected the shape and height of the peak, thus effectively lowering the sensitivity of the system.

Using this setup, sensitivities to about 1 p.p.b. of SF_6 in air were obtained. Figure 2 shows one of the calibration curves. SF_6-air mixtures for calibration were made up by the double dilution system previously described (Collins, Bartlett, *et al.*, 1965). The calibration sample was transferred from the

dilution system into a stainless steel tank, and then was pressurized with air that had been purified as previously described.

This analytical procedure is suitable for routine use with ambient air samples taken under conditions of typical New York or Connecticut summer temperatures and humidities. The moisture is retained on the silica gel column during the analysis of as many as about 50 5-ml. samples. Under these circumstances, reconditioning of the column for removal of water can be programmed during the night without encroaching on the time used for analysis.

Concentration Procedure

For SF_6 concentrations less than about 1 p.p.b., the direct technique described above is not sufficiently sensitive. In such cases, the analytical signal can be recovered by concentrating the SF_6 in several liters of sample into a small volume. To do this, the 5-ml. stainless steel sampling loop of the gas sampling valve is bent into a U-shape so that when it is immersed in refrigerant contained in a Dewar flask, it serves as a

Figure 2. Calibration curve for SF_6 in air

Figure 1. Typical response from mixture of SF_6 and air

Approximate SF_6 concentration, 8 p.p.b.

freeze-out trap. The inlet and outlet of the gas sampling valve are fitted with needle valves so that the sampling loop can be sealed off. The outlet is also fitted with a rotameter and a wet-test meter. The pressurized tank is then connected as previously described. After flushing the trap several times with the sample, both needle valves are closed and the trap is cooled with liquid oxygen (not liquid nitrogen, which will lead to dangerously high pressures when the trap is warmed). The valves are then opened, and the sample is passed through the trap at a maximum rate of 500 ml. per minute. If this rate is exceeded, not all the SF_6 in the sample is condensed. Since a 1000-cu. inch tank pressurized to 45 p.s.i.g. will release more than 40 liters of sample, this concentration procedure will allow sensitivities of more than 2000 times the direct method of analysis. The wet-test meter measures the total sample. When the desired sample volume has been concentrated, the needle valves are again closed, the loop is warmed with water, and the sample is introduced into the chromatograph.

This concentration procedure is independent of the chro-
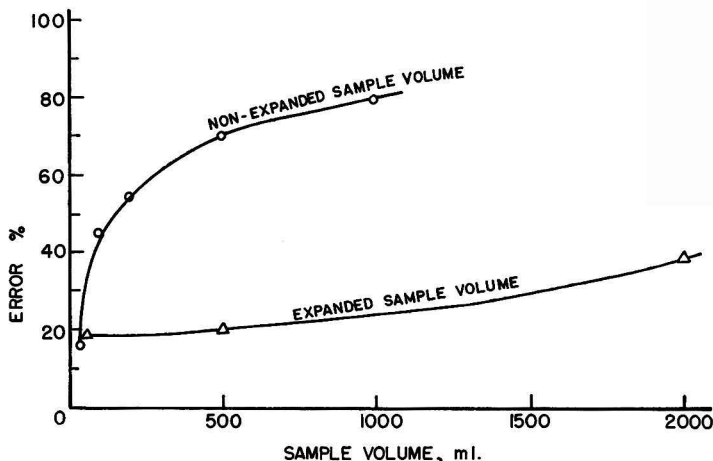
Figure 3. Calculated maximum errors in concentration procedures
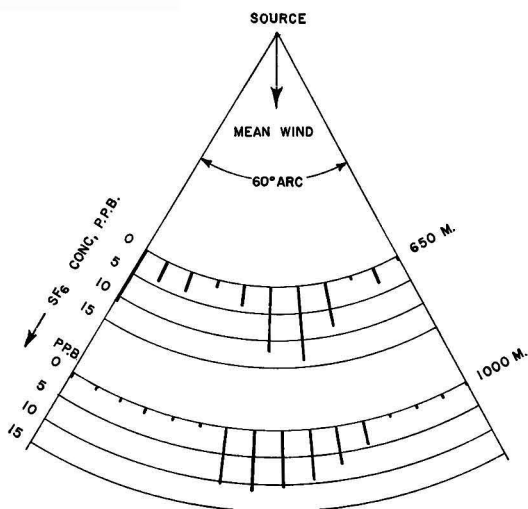
Figure 4. Plume profile during field test

matographic system, and can therefore be used to enhance the response of any analytical procedure for SF_6.

Recovery Analysis

The maximum error in a dilution procedure can be calculated on the following basis. Assume that an initial concentration of vapor, C_i, is sufficiently high so that it can be determined accurately by a reliable method of analysis. The vapor is then diluted by a factor, F_d, that is nominally determined by volume or flow ratios in the system, to a lower concentration, C_d. Now, using some method such as freeze-out trapping, the diluted vapor is reconcentrated by a factor, F_r, to recover a high concentration, C_r, which, like C_i, can be determined accurately. Now the value for the concentration of the diluted vapor that is calculated without a confirming analysis from the applied dilution factor is

$$C_{d(calcd)} = C_i F_d$$

The reconcentrated value is

$$C_r = C_d F_r, \text{ and } C_d = C_r / F_r$$

Now, the error in measuring C_d is

$$\text{Error (fractional)} = \frac{C_{d(calcd)} - C_d}{C_{d(calcd)}} = \frac{C_i F_d - C_r / F_r}{C_i F_d}$$

$$= 1 - \frac{C_r}{C_i F_d F_r}$$

If $F_d = 1/F_r$—that is, if the original concentration is nominally restored after dilution—then error $= 1 - C_r/C_i$. In this calculation, recovery of the diluted vapor is assumed to be complete, and all of the error is assumed to lie in the dilution

Table I. SF₆ Background Concentrations in Manhattan[a]

Locations near Power Station	Concentration, P.P.B.
On roof of church on south side of 13th Street, midway between C and D	0.09
Power station control room	0.07
North side of 13th Street between Avenues C and D, near D	0.40
North side of 13th Street between Avenues C and D, near C	0.01
On top of transformer in approximate center of power station	0.06
Northeast corner of 13th Street and Avenue D	0.00
Southeast corner of 14th Street and Avenue D	0.06
Locations not near Power Station	
5th Avenue between 54th and 55th Streets	0.01
In Central Park at about 60th Street	0.01
In Central Park at about 82nd Street	0.00
Southwest corner of 106th Street and 5th Avenue	0.00
103rd Street and Riverside Drive	0.00

[a] Container backgrounds may be as high as 0.01 p.p.b.

procedure. If some loss occurring during reconcentration is thus erroneously ascribed to the dilution, then the calculated dilution error is too high. There is no way to resolve the question except to state that the calculated error is a maximum value, and that the real error therefore cannot be any greater than that obtained by this procedure.

Data obtained from the application of this recovery analysis to the concentration technique described are illustrated by the upper curve of Figure 3. The probable cause of these extreme errors was determined to be loss of sample through leaks in the gas sampling valve due to a pressure increase in the valve when the concentrated sample is rewarmed. To minimize this loss of sample, the concentration procedure was modified by providing an 8-ml. expansion chamber that decreases the pressure buildup on the valve. The result is a sharply decreased loss of sample, as is shown by the lower curve of Figure 3. The important point is that if the recovery analysis had not signaled the loss, it would not have been detected or remedied. These curves do not extrapolate to zero error, indicating another loss of sample, comparatively independent of total pressure. The source of this loss might be adsorption on the walls of the container.

SF₆ Backgrounds

Sulfur hexafluoride is used industrially as an insulating material in high voltage transformers and circuit breakers. Therefore, background levels should be checked when work is contemplated near sites where such units are likely to be found. For example, samples were taken near the Consolidated Edison power plant located in Manhattan, New York, N. Y., at 14th Street between Avenues C and D, where SF₆ is used

as an insulator for circuit breakers. The results of these tests are listed in Table I. Other samples taken at random locations in Manhattan are also shown. The backgrounds, especially near the power station, are sufficiently high to be a problem if tracing is done over any considerable distance, where large dilutions and consequent low concentrations can be expected.

Another problem inherent in the concentration technique is sorption and desorption of SF₆ on the walls of the container. New containers, never used for SF₆, are free of any contamination .Previously exposed containers, however, can be a source of SF₆ backgrounds. Glass is an offender in this respect, the persistent steady-state concentration from previously contaminated glass being greater than 13 p.p.b. This high value makes glass completely unsuitable for static retention of SF₆ (although it is suitable for dynamic systems). Saran bags gave responses of approximately 0.2 p.p.b., making them suitable containers for re-use if the tracing is done at sufficiently high levels. Stainless steel tanks gave the lowest concentrations of all the materials tried; approximately 0.01 p.p.b. This allows for almost a 100-fold increase in sensitivity by concentrating the sample. The stainless steel containers are most conveniently cleaned by flushing them with air that has been purified in the manner previously described. The flushed containers are then evacuated.

Gas Tracing of a Stack Effluent

The SF₆ tracer method was used in a test of stack effluent dilution conducted on February 17, 1966, in Barrington, N. J., in cooperation with the N. J. State Department of Health and the Owens-Corning Fiberglas Corp.

Test Site. The tracer source was an industrial stack, rising from a roof at 18 meters to a height of 41 meters above ground level (see Figure 4). Stack gas emission rate was 4070 cu. meters per minute, emerging at a temperature of 135° F. and an exit velocity of 1400 meters per minute.

Meteorological Conditions. The weather was clear. The average wind speed was 14 knots, with occasional gusts to 29 knots; the average wind direction was 304 degrees, with a range of 260 to 330 degrees. Atmospheric stability was close to neutral, there being no temperature change with elevation. Under the prevailing conditions, the plume was immediately deflected downward because of the aerodynamic downwash caused by an adjacent structure. The average point of plume touchdown was estimated to be about 4 stack heights from its source, or about 170 meters.

SF₆ Tracer Gas Injection. Tracer gas was injected from 8:40 A.M. to 9:24 A.M. into a ³/₈-inch line which ran from the SF₆ cylinder, through a rotameter at roof level, and to a point of penetration about halfway up the stack. The rate of gas introduction into the stack was 0.1325 cu. meter per minute, corrected for 40° F. and a back pressure of 15 p.s.i.g.

Sampling and Analytical Findings. Samples were collected at each of 27 stations (Figure 5) from approximately 9:00 A.M. to 9:20 A.M. during the passage of the SF₆ cloud. The stations were uniformly distributed along each of two 60°
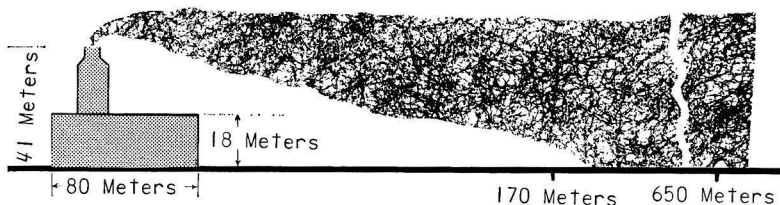
Figure 5. Dispersion of SF₆ discharge from stack during field test

arcs, symmetrically oriented along the plume center line, one at 650 meters and the other at 1000 meters from the source. Samples were collected in 1000-cu. inch stainless steel tanks equipped with valves and constant differential–type flow controllers. Samples were collected 2 meters above ground level over the entire 20-minute period at the uniform rate of 0.028 cu. meter per hour. The results of the SF₆ analyses shown in Figure 5 present a rational dispersion pattern with the exception of some high values at one side of the inner arc, which might have been the result of a puff detached from the main cloud. The plume centerline is delineated well. The average ground level concentration of SF₆ along the plume axis at 650 meters from the source was 14.2 p.p.b. The concentration in the stack was 32,500 p.p.b. Hence, the dilution factor was 2290.

Comparison of Results Obtained from Gas Tracer with Meteorological Calculations.

$$\text{Concn. of SF}_6 \text{ in stack} = \frac{\text{SF}_6}{\text{total effluent}}$$

$$= \frac{0.1325 \text{ cu. meter per min.}}{4078 \text{ cu. meters per min.}} \times 10^9$$

$$= 32{,}500 \text{ p.p.b.}$$

Observed dilution factors, referred to plume center line:

$$\text{Dilution factor} = \frac{\text{stack concentration}}{\text{observed downwind concentration}}$$

$$(\text{At 650 meters}) = \frac{32{,}500 \text{ p.p.b.}}{14.2 \text{ p.p.b.}} = 2290$$

$$(\text{At 1000 meters}) = \frac{32{,}500 \text{ p.p.b.}}{11.1 \text{ p.p.b.}} = 2930$$

The downwind ground level concentrations at plume centerline was computed from the equation of Pasquill (1962).

$$\text{Concn.} = \frac{Q}{2\pi \bar{u} \sigma_y \sigma_z} e^{-1/2 H^2/\sigma_z^2}$$

where Q = emission rate of SF₆ (cu. meters per second)

$\bar{u}$ = average windspeed (meters per second)

σ_y, σ_z = lateral and vertical diffusion parameters (meters)

H = stack height (meters)

Assuming a straight line distance from the stack to the centerline of the plume on the 650-meter arc, the solution of the equation gives:

$$\text{Concn.} = \frac{0.0022}{2\pi(8.0)(58)(35)} \, {}^{-1/2(41)^2/(35)^2} = 21.4 \text{ p.p.b.}$$

Observed value at 650 meters = 14.2 p.p.b.
From similar calculation at 1000 meters,

Calculated concn. of SF₆ = 12.0 p.p.b.

Observed value at 1000 meters = 11.1 p.p.b.

In predictions of this type, results within a factor of two of the calculated value are considered excellent.

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Chemical Interactions in the Aggregation of Bacteria
Bioflocculation in Waste Treatment

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■ Aggregation of microorganisms is effected by an interaction of polymers excreted by the microbial cell or exposed at their surface. This proposition has been tested by demonstrating that bacteria can be flocculated with synthetic anionic and nonionic polyelectrolytes (polyacrylamide, polystyrene sulfonate, polyglutamic acid, and dextran). As with hydrophobic sol–polymer systems with charges of equal sign, reduction of surface potential is not a prerequisite for flocculation; agglomeration apparently results from specific adsorption of polymer segments and from bridging of polymers between the cells. Extracellular or cell surface polymeric material isolated from cell-free supernatant of a well flocculating activated sludge culture is, similar to synthetic polyelectrolytes, capable of destabilizing dispersions of bacteria and of abiotic sols.

M any microorganisms have a tendency to adhere to interfaces and to each other; under certain conditions they remain freely dispersed; under others they form aggregates. Microbial aggregation influences the temporal and spatial distribution of nutrients in aquatic habitats. Flocculation is of significance in biological waste treatment. The efficiency of the conventional activated sludge process greatly depends upon bioflocculation and subsequent phase separation of the flocs from the treated effluent.

Natural polymers are of great importance in sorptive and colloidal destabilization reactions in biological systems. For example, the reaction between antibody and antigen (Goldberg, 1952; Katchalsky, Danon, *et al.*, 1959), the cohesion of tissue cells (Pethica, 1961; Moscona, 1962), the aggregation of sponge cells (Humphreys, 1965), the flocculation of yeast cells (Mill, 1964), and the stabilization of soil aggregates (Greenland, Lindstrom, *et al.*, 1961) have been interpreted in terms of colloid-polymer interactions. Similarly, Tenney and Stumm (1965) have proposed that flocculation of microorganisms in biological waste treatment is effected by an interaction of polymers excreted by the microorganism or exposed at the microbial surface under suitable physiological conditions. According to this hypothesis, flocculation of the dispersed organisms is interpreted as a process whereby polymers adsorb to and bridge between cell surfaces.

This research was undertaken to provide experimental corroboration for a polymer mechanism in bioflocculation and a better understanding of some of the factors that influence aggregation of microorganisms and other colloids in biological waste treatment.

Bacteria as Hydrophilic Colloids

Within the pH-range of interest (pH 5 to 9), bacteria carry a net negative charge resulting from acid-base ionization of functional groups in the bacterial surface. Because of the hydrophilic surface, the stability of a bacterial dispersion does not primarily depend on the electrostatic repulsive forces between the cells. Reduction of surface potential is not a prerequisite for bioflocculation; bacterial suspensions can form stable dispersions even at the isoelectric point (pH 2 to 3 for most bacteria). Electrolyte concentrations capable of coagulating hydrophobic sols have no effect in destabilizing bacteria. The cell-free supernatant of a bacterial culture, presumably containing material excreted by the organisms or sheared off the cell surface, is capable of imparting a negative electrophoretic mobility to incipiently positively charged Al_2O_3. It may be inferred that polymeric material excreted or exposed at the surface of microorganisms contains functional groups that are primarily anionic and nonionic in the neutral pH range. Therefore, if aggregation of bacterial cells is assumed to result from polymer interactions, the anionic and nonionic polymeric cell products must be capable of interacting with the negatively charged bacterial surface.

To test the proposition that specific chemical interactions can occur between bacterial surfaces and polymers which are not opposite in charge characteristics, it appeared desirable to validate experimentally that microorganisms can be flocculated by synthetic anionic and nonionic polyelectrolytes and to show that extracellular polymeric material produced by the cell has flocculative properties similar to those of synthetic polyelectrolytic flocculants.

Materials and Methods

Polyacrylamide, polystyrene sulfonate, and polygalacturonic acid and dextran were supplied by American Cyanamid, Dow Chemical Co., and Sigma Chemical Co., respectively. The bacteria used for pure culture experiments were obtained from the American Type Culture Collection.

The methods employed in this investigation have been described in detail by Busch (1966). A continuous supply of bacteria of similar physiological state and similar surface characteristics was maintained by a 500-ml. single-stage continuous culture apparatus, using incipiently sterile media containing glucose or benzoate as carbon sources. Dilution rates in most experiments were between 0.5 and 0.8 hour^{-1}.

Various methods of measuring bacterial aggregation (counting microscopically or electronically, settling, cake filtration, and light scattering) have been compared (Busch, 1966);

no method tested was entirely adequate; light scattering intensity, τ, (the ratio of the intensity of light scattered at 90° to the light transmitted) was considered most satisfactory although not always sensitive. While not quantitative, light scattering results do present a qualitative measure of aggregation while requiring no sample dilution or extensive measurement times. A reduction in τ indicates an increase in aggregation at constant weight concentration of particles. For comparative purposes the relative scattering intensity τ/τ_0 is used to indicate a change in aggregation; τ_0 is the light scattering intensity of a reference sample—e.g., sample without polymer added. Measurements of τ were made at 546 mμ (Brice Phoenix light-scattering photometer) 20 minutes after addition of polymer and subsequent slow stirring of the bacterial-polymer dispersion.

Material containing cell-free flocculants was isolated from the supernatant of a well flocculating activated sludge culture maintained in the laboratory. The bacteria in this culture were concentrated by gravity sedimentation for 1 to 2 hours. The heavy sludge that resulted was centrifuged at ca. 24,000 G. The supernatant from this centrifugation was added to an ethanol solution (3 parts ethanol for 1 part supernatant). The precipitate which developed was centrifuged and resuspended in an ethanol-water solution (3 to 1) three times and finally air-dried.

Results and Discussion

Flocculation of Bacteria with Synthetic Anionic and Nonionic Polyelectrolytes. Several representative flocculation curves describing the aggregation of *Aerobacter aerogenes* or *Escherichia coli* with various polyelectrolytes are given in Figure 1. These curves are typical; at polymer concentrations larger than those required for optimum flocculation, redispersion or restabilization of the bacterial suspension occurs. As illustrated in Figure 1a, the electrophoretic mobility, reflecting a negative surface potential on the bacterial interface, becomes more negative as a result of the addition and subsequent adsorption of the anionic polyelectrolyte.

Similar experiments were also conducted with polyglutamic acid and with dextran. Polyglutamic acid produced flocculation at a pH of ca. 4. At this pH, the polyglutamic acid molecule has a net charge of zero. Bacterial aggregation with nonionic dextran (M.W. = 6,000,000) occurs, however, with very little efficiency at a pH optimum of approximately 5.

The forces responsible for attachment of the polyelectrolyte segments to the bacterial surfaces appear to be relatively weak, since increased agitation (stirring at >30 r.p.m. with magnetic stirring bars) results in shear forces that disperse the aggregates. The pH of the medium has a rather pronounced effect on the efficiency of the aggregation. Different polymers require different pH optima; no satisfactory explanation for these pH effects can be given.

The phenomena involved in the flocculation of colloidally dispersed hydrophobic solids by polyelectrolytes has been interpreted satisfactorily as a process of specific adsorption of polymers or polymer segments on the colloidal surface
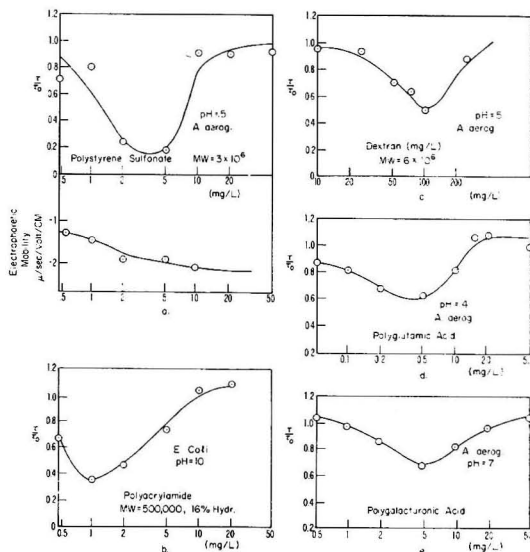
Figure 1. Aggregation and redispersion of bacteria by anionic and nonionic polymers

a,b,e. Anionic polyelectrolytes *c.* Nonionic polysaccharide *d.* Polyglutamic acid has no net charge at pH-4

leading to bridging of polymer chains between solid particles (Ruehrwein and Ward, 1952; Michaels, 1954; Smellie and LaMer, 1958). The effect of polyelectrolytes on hydrophilic colloids such as bacteria may be explained similarly. In accordance with such a model, optimum destabilization occurs when a certain fraction of available adsorption sites on the surface of the bacteria are bridged by polymers. Correspondingly, the optimum polymer dose should be proportional to the colloid concentration, or more exactly, to the available surface area. Such a linear relationship has been observed in this investigation (Figure 2). When polymer concentrations exceed this optimum, bridging is limited and cells become redispersed since many of the reactive surface sites are occupied by polymers, which are then unable to find unfilled sites on other colloids or are hindered by steric (Heller and Pugh, 1960) or electrostatic (LaMer and Healy, 1963) interferences between polymer segments.

In this theory, polyelectrolyte segments must be held on the bacterial surface by forces that can outweigh those of purely electrostatic origin. Possible mechanisms for the attachment of anionic functional groups to negatively charged surfaces are: hydrogen bonding; anion interchange with adsorbed anions (such as OH⁻); or interactions with cations on or in the immediate vicinity of the bacterial surface. Flocculation of a polymer-sol system with charges of equal sign occurs only if an appropriate concentration of an electrolyte is present in the solution (Overbeck, 1938; Deveaux, 1939; Black, Birkner, *et al.*, 1966; Sommerauer, Sussman, *et al.*, 1967; Nemeth and Matijević, 1967). However, flocculation with polyelectrolytes can occur at electrolyte concentrations much smaller than those necessary for flocculation in the absence of polymers. In these investigations, satisfactory flocculation with polymers was observed only when the concentration of divalent cations

exceeded a certain minimum (for example, $3 \times 10^{-4} M$ of Ca^{+2} or Mg^{+2}). In the absence of polymers, bivalent ion concentrations larger than $10^{-1} M$ produced aggregation. In accordance with earlier investigations on the effect of electrolytes on the stability of a hydrophobic negative sol–anionic polymer system (Sommerauer, Sussman, *et al.*, 1967), the authors believe that the primary role of divalent cations in the flocculation of bacteria is complex or ion pair formation between the functional groups of the polyelectrolyte and the "counter ion" in the immediate vicinity of the bacterial surface, thus enhancing the adsorption of polymer segments at the interface. Although concentrations of bivalent cation and polymer are not sufficiently high in the bulk solution to lead to complex formation, coordination becomes possible in the vicinity of the negatively charged bacterial surface where, for electrostatic reasons, incipient cation concentration is much larger than in the bulk of the solution.

Flocculation with Polymers of Bacterial Origin. Material containing cell-free flocculants was isolated by ethanol precipitation from the supernatant of a centrifuged activated sludge culture fed on glucose. This precipitate presumably contained some of the capsular substances loosely bound to the microbial surface and other natural polymers that might have been excreted by the organisms. Analysis of the precipitate revealed no appreciable quantities of nucleic acids or protein, but the material gave a positive anthrone test indicative of carbohydrates. An aqueous solution of this material was capable of imparting a negative electrophoretic mobility to Al_2O_3 particles of incipient positive surface potential at a pH of 7 indicating that the interfacially active components in the cell free supernatant were anionic in the neutral pH range.

These components are also capable of flocculating inorganic colloidal dispersions with a negative surface potential. Figure 3 shows typical flocculation-redispersion curves for silica and for *A. aerogenes*. An electron micrograph of a representative silica floc taken from this experiment is shown in Figure 4. The spacing between the individual particles is relatively uniform and rather large (100 to 1000 Å.). The fact that similar intraparticular distances have been reported for the aggregation of cells by biological polymers (Ambrose, 1964; Humphreys, 1965; Pethica, 1961) is suggestive.

The material containing the natural polymers is also capable of aggregating suspensions of dispersely growing *A. aerogenes* (Figure 3,*b*). This flocculation curve is similar to the curves describing the interactions between synthetic polyelectrolytes and negatively charged colloids.

The observation that extracellular products of the organisms can change the stability of dispersed cells and inorganic sols in a similar manner suggests that these polymers may also form bridges between cells and other solids thus coflocculating inorganic colloids and bacterial cells. Figure 5 shows that the flocculative removal of dispersed silica from solution is enhanced by the addition of well flocculating bacteria.
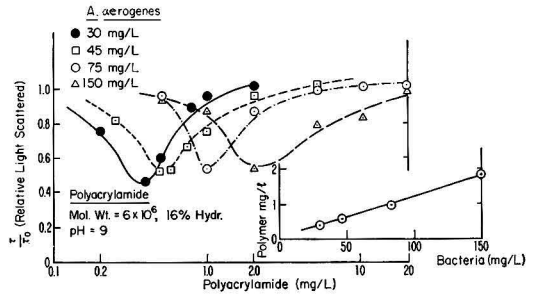
Figure 2. Relation between concentration of bacteria and the optimum dosage of polyacrylamide
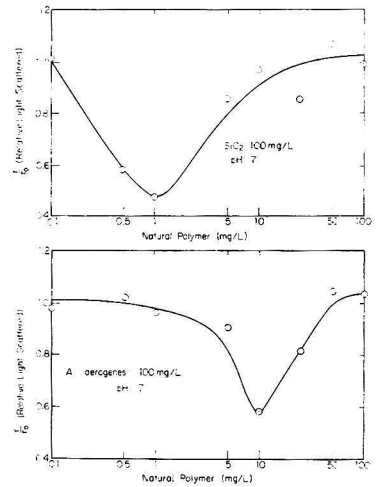
Figure 3. Aggregation of SiO$_2$ (Min-U-Sil, 5) and of *A. aerogenes* with polymers of bacterial origin

Figure 5. Flocculating bacteria enhance the removal of SiO_2 particles

Figure 4. Electron micrograph of particles aggregated with polymers of bacterial origin

Bioflocculation. Uncertainty exists regarding the mechanism of natural bioflocculation in biological waste treatment. The various mechanisms that have been proposed have been reviewed recently by Crabtree, Boyle, *et al.* (1966).

A typical biological floc consists of a great variety of bacteria and occasionally other organisms such as protozoa, fungi, and viruses, as well as abiotic suspended matter. Thus, a floc may comprise a broad spectrum of hydrophobic and hydrophilic interfaces. Proteins, lipides, and polysaccharides combined in various proportions occur on the surfaces of microorganisms in the form of cell walls, capsules, flagellae, fibrils, filaments, and fimbriae of various kinds. The morphological appearance of the floc depends in a complex way on the structure of the microbial population and the nutritional conditions in the medium. Bioflocculation results from complicated physical, chemical, and biological interactions; many variables, difficult to control experimentally, are involved. Different mechanisms of floc formation may be operative for biological flocs originating from different organisms or combinations of organisms; a few strains of microorganisms may remain dispersed in the presence of excess polymer and may flocculate only after the excess has been removed. No single and unifying interpretation can be given.

Bioflocculation is strongly influenced by the growth phase of the microorganisms; generally, the tendency for bioflocculation is larger under conditions of declining or endogenous growth than under conditions of prolific growth. Some strains of microorganisms are known to synthesize extracellular polysaccharides or other polymers, especially under conditions where growth is limited by a nutrient other than carbon—e.g., nitrogen. The chemical transformations and condensations necessary for synthesis of polymers demand little energy and can be carried out by the cells even in the absence of growth. However, since most municipal wastes are nutritionally deficient in carbon (atoms $C/N < 5$), other nutrients (N, P) are usually not growth limiting in biological waste treatment. Extensive bioproduction of polymers in large quantities is less likely to occur under such conditions. Nevertheless, cell binding polymeric material conducive to flocculence may also be produced under declining or endogenous carbon limited growth. Perhaps an adequate concentration of polymer can accumulate per unit surface area only under conditions of declining or endogenous growth. While organisms are growing prolifically, new microbial

surfaces are produced faster than surfaces can become covered with polymers.

According to this simple picture, newly formed cells remain dispersed as long as they replicate rapidly; thus, in the presence of sufficient metabolites, dispersed bacteria outgrow flocs. If growth becomes very slow or ceases—i.e., under conditions of long detention time in continuous culture or biological treatment systems—the "old" not readily replicating cells adhere to each other and form aggregates. Furthermore, because settleable organisms are recirculated, flocculating cells are selectively retained in the activated sludge tank, while dispersed cells are washed out of the system.

Practical Aspects. In aerobic biological treatment of waste, there is an incompatibility between the requirements for large specific substrate utilization rates (high growth rate, small detention times) and the requirements for maximum bioflocculation (small growth rates, large detention times). In treatment processes with submerged flocs (activated sludge), the rapid removal of organic matter during the initial contact period (the so-called contact stabilization) may, at least to a large part, be attributed to the flocculation of colloidal and macromolecular organic substances. Addition of suitable chemical flocculants, or control of the chemical parameters which affect natural aggregation, are among the possibilities for improving the efficiency of bioflocculation. Natural polymers isolated from well flocculating bacteria or from "slime" producing algae or other plant biocolloids may be more expedient flocculants than the synthetic polymers used in this and an earlier study (cationic flocculants; Tenney and Stumm, 1965).

Conclusions

In this investigation, the authors have attempted to approach only the issue concerning the nature of the interactions of the cells with each other and with other interfaces. The results presented appear to confirm the general working concept that polymeric extracellular or cell-surface material is involved in bacterial aggregation. The interaction forces operative in biological self-flocculation appear to be stronger than those encountered in the aggregation by synthetic polyelectrolytes. Bioflocs are not as sensitive to dispersion by shear forces as bacterial aggregates flocculated by synthetic polymers. Natural flocs also are not so critically dependent on pH and polymer concentration. Little is known of the chemical nature of flocculent material produced by the cell. Quite likely different organisms produce different cell binding materials; these may be of low molecular weight and soluble or of high molecular weight with a high degree of crosslinkage and exist as a rather "gelatinous slime." The molecular framework may in many cases be comprised of polymeric carbohydrates containing anionic and nonionic functional groups, such as $-COO^-$ and $-OH$ groups. The fact that synthetic polymers containing similar anionic ($-COO^-$ and $-SO_3^-$) and nonionic ($-OH$) groups are able to aggregate organisms is considered a valid demonstration that natural anionic polymers may, under suitable conditions, become specifically adsorbed at microbial surfaces and thus able to form bridges with adjacent surfaces leading to aggregates. This hypothesis is further reinforced by the observation that interfacially active anionic material precipitated from a cell-free supernatant of a flocculating activated sludge culture can destabilize dispersions of bacteria and of abiotic sols.

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Tertiary Treatment of Municipal Sewage Effluents

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■ A modification of the Desal process for treatment of brackish waters is effective for renovating secondary sewage effluents producing completely clarified, odor-free water. The treated waters exhibit a reduced over-all mineral solids content and contain very low levels of refractory organics. The renovated effluents appear to meet many of the requirements needed for a water to be useful, at least for agricultural or industrial purposes.

The mineral composition of sewage can be very varied, being dependent primarily upon the original composition of the municipal water supply and on the mode and extent to which the water has been utilized by the community. With each water-use cycle there is an incremental buildup of dissolved inorganic salts. In addition, other materials foreign to the original water are introduced. Principally through the use of synthetic detergents, there is a substantial increase in the phosphorus content and the methylene blueactive substances (MBAS). The principal cations in these waters are Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}, while the principal anions are Cl^-, HCO_3^-, SO_4^{2-}, NO_3^-, and phosphates. Frequently, chloride and bicarbonate salts predominate.

Though the Public Health Drinking Water Standards do not place quantitative limitations on certain components which contribute to chemical oxygen demand (COD), biochemical oxygen demand (BOD), etc., it is well realized that elevated concentrations of these components should be avoided. Phosphates and nitrates act as nutrients in stimulating undesirable aquatic growth; MBAS are esthetically undesirable, since they give rise to excessive foaming when present in concentrations as low as ∽0.5 to 1.0 p.p.m. Though NH_4^+ is apparently not of immediate concern from a health viewpoint, it is nevertheless desirable to eliminate most of this constituent in order to keep chlorination costs down. Since typical municipal waste water may contain as much as 20 p.p.m. of NH_4^+, most of the NH_4^+ must be removed when the water is destined for human consumption. Even simple inorganic salts can pollute water if present in sufficiently high concentrations. For this reason, Public Health Service Drinking Water Standards recommend that the total dissolved solids in drinking water should not exceed 500 mg. per liter.

Only a few of the organic materials present in sewage waters have been identified. Besides linear alkylate sulfonates (LAS), other organic substances that may be found are carbohydrates, fatty acids, and proteins.

For an advanced waste treatment process to be acceptable for the ultimate purification of sewage plant effluents for municipal use, certain requirements must be met. The proposed process should be able to: reduce the soluble organic and inorganic ionic species to a suitable level; eliminate or modify objectionable ions; soften the water to within tolerable levels; effect an over-all reduction of BOD and COD to a level comparable with that of average tap waters; significantly lower the surfactant (MBAS) level to a point where foaming is no longer a problem; render the water free of pathogens and make it esthetically acceptable; and accomplish these results at processing costs that are not so prohibitively high as to render the process unsound from an economical standpoint.

The aim of our tertiary treatment studies has been the development of a process capable of purifying these wastes. During the studies, a most effective process for renovating secondary sewage effluents was a modification of the Rohm and Haas Co. Desal process (Kunin, 1963, 1964), developed primarily for the desalination of brackish waters. The principal reactions involved in the process, assuming for simplicity that the sewage contains primarily monovalent salts, are:

$$(R\text{—}N) + H_2O + CO_2 \rightarrow (R\text{—}NH)HCO_3 \text{ (carbonation)} \quad (1)$$

$$(R\text{—}NH)HCO_3 + NaCl \rightarrow (R\text{—}NH)Cl + NaHCO_3$$
$$\text{(alkalization)} \quad (2)$$

$$R\text{—}COOH + NaHCO_3 \rightarrow R\text{—}COONa + CO_2 + H_2O$$
$$\text{(dealkalization)} \quad (3)$$

$$(R\text{—}NH)Cl + NH_4OH \rightarrow (R\text{—}N) + NH_4Cl + H_2O$$
$$\text{(anion exchanger regeneration)} \quad (4)$$

$$2 R\text{—}COONa + H_2SO_4 \rightarrow 2 RCOOH + Na_2SO_4$$
$$\text{(cation exchanger regeneration)} \quad (5)$$
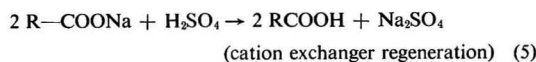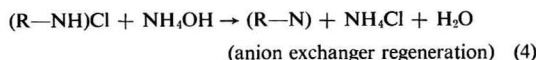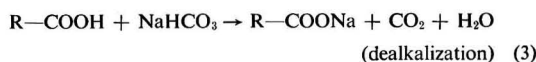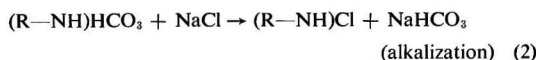
In the optimized process, a weak-base anion exchange resin is initially converted to the bicarbonate form (Equation 1) and then the secondary sewage is treated by the resin (Equa-

tion 2) to convert the inorganic salts present in the sewage to bicarbonate salts. During the alkalization step, considerable adsorption of organic matter by the resin also occurs. After the alkalization step, the alkalized sewage is subjected to a flocculation treatment, aerated, and then lime-softened. Additional organic matter is precipitated from the sewage and a large portion of the Ca^{2+} and Mg^{2+} hardness is removed through the formation and precipitation of the relatively insoluble carbonates and hydrous oxides. Complete turbidity and odor removal is also achieved. The treated secondary sewage may be subsequently dealkalized (Equation 3) using a weak cation exchange resin to reduce the dissolved salt content further and to remove any ammonia that might be present. The anion exchange resin is treated with normal aqueous ammonia (Equation 4) and the cation exchange resin with normal aqueous acid (Equation 5) during regeneration.

Experimental

Ion Exchange Resins and Coagulants. In the alkalization unit, Amberlite IRA-68 (Rohm and Haas Co.) was used exclusively. This compound is a weak-base polyamine anion exchange resin based on an acrylic structure which can be operated very efficiently in the bicarbonate cycle. The resin in question has a volume anion exchange capacity of 1.63 meq. per ml.

Amberlite IRC-84 (Rohm and Haas Co.), a carboxylic cation exchange resin, also based on an acrylic structure, was used in the dealkalization unit. Operated in the hydrogen cycle, the resin has a volume cation exchange capacity of approximately 4.5 meq. per ml. Primafloc C-7 (Rohm and Haas Co.) was the synthetic organic cationic polyelectrolyte used during the flocculation step of the process. It is a straight-chain water-soluble cationic polymer of very high molecular weight. In these studies it was used as a 0.1% (product basis) solution. KWK Volclay (American Colloid Co.) bentonite was used as a 1% aqueous suspenson in conjunction with the Primafloc C-7 during the flocculation step. A lime of commercial grade was applied as a 3.6% aqueous suspension during the lime-softening operation.

Secondary Sewage Effluent. All of the processing studies were conducted on a laboratory scale using chlorinated secondary sewage effluent from the Haddonfield, N. J., waste disposal treatment plant. The Haddonfield plant treatment process consists basically of primary treatment, secondary treatment (activated sludge), and chlorination. Table I lists some of the principal properties and compositions of the particular water with which most of our column studies were performed. Sewage effluent waters sampled at different periods of time showed a remarkable constancy in ionic composition, though some variations were noted in the organic content. The presence of ammonium ions and the low nitrate value suggest that the secondary treatment process was not being operated under optimum nitrifying conditions.

Apparatus. The alkalization step was performed in a pressurized ion exchange unit and upflow to minimize pressure-drop difficulties that might have occurred had conventional downflow practices been employed. The unit could be operated up to 75-p.s.i. pressure (Figure 1). During regeneration, the configuration of the equipment allowed for both NH_4OH regeneration under gravity flow and carbonation of the anion exchanger under pressure. The column was approximately

Table I. Composition of Haddonfield, N. J., Chlorinated Secondary Effluent

pH	7.80
Specific resistance, ohm cm.	1700
MBAS, p.p.m.	2.0
COD, p.p.m.	90
Hardness, p.p.m. as $CaCO_3$	98
NH_4^+, p.p.m. as $CaCO_3$	50
Cl^-, p.p.m. as $CaCO_3$	45
NO_3^-, p.p.m. as $CaCO_3$	1.5
Orthophosphates, p.p.m. as $CaCO_3$	33
Alkalinity, MO, p.p.m. as $CaCO_3$	160
Total anions, p.p.m. as $CaCO_3$	260

36 inches long and had an internal diameter of 1 inch and was fitted with two stainless steel fine-wire-mesh screens at both ends. Using a 200-ml. resin bed volume, enough head room was available in the column to allow for at least 100% expansion of the bed during the upflow exhaustion cycle. When the resin was regenerated with NH_4OH, the column was isolated from the rest of the system by manipulating the appropriate valves. Two plugs at the ends of the column were removed and regeneration was then performed by gravity. The carbonation step was performed under pressure. After 2-liter volumes of water had been introduced into the autoclave, CO_2 was percolated into the water under a 75-p.s.i. pressure for approximately 10 minutes. The carbonated water was next passed (downflow) through the pressurized column using a 50-p.s.i. CO_2 head pressure. Once regenerated, the secondary sewage effluent water was introduced into the autoclave and in turn passed upflow through the column, again using a 50-p.s.i. CO_2 driving pressure.

The flocculation and lime-softening steps of the process were conducted using a standard jar testing apparatus (Phipps and Bird, Inc.). In the laboratory, the flocculation, aeration, and lime-softening steps were performed in a single vessel, though on an industrial scale it might be preferable to perform the operations in multiple units. In the flocculation step, the effluents emerging from the alkalization unit were given
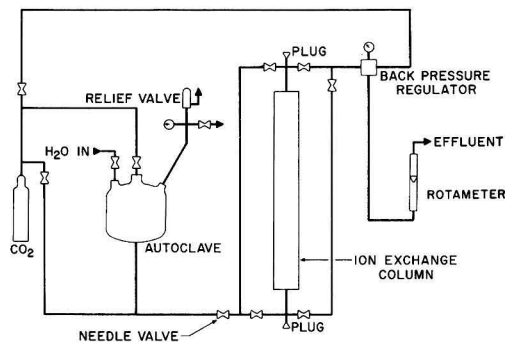
Figure 1. Schematic drawing of pressurized ion exchange system for treatment of secondary sewage effluent

a bentonite–Primafloc C-7 treatment to remove organic matter which failed to be adsorbed by the alkalization unit.

After the flocculated waters had been aerated to expel free CO_2, a cold lime-softening treatment was performed. A quantity of lime chemically equivalent to the initial hardness of the secondary effluent prior to treatment was used, applied as a 3.6% aqueous suspension.

The dealkalization unit contained the cation exchange resin and was operated in the hydrogen cycle. In the modified process, the dealkalization unit need not be pressurized, since it further polishes the renovated secondary sewage water in order to effect additional solids reduction and softening if required. In the laboratory, a 50-ml. buret column containing 25 ml. of the hydrated resin was used effectively under gravity flow. The position of the dealkalization unit in the Desal process for secondary sewage water renovation is shown in Figure 2.

Analysis. The progress of the alkalization step of the process was followed by evaluating bed volume fractions of effluent water emerging from the anion exchange resin unit. Chloride and methyl orange (MO) alkalinity were determined for each of the fractions, and breakthrough was taken as a point where 50% chloride leakage was observed. Total cations in the influent sewage and in the final processed waters were obtained by passing appropriate size samples through a small column containing Amberlite IR-120 (H). After the effluents were collected, they were titrated to the methyl orange end point with $0.1N$ NaOH and the values related to the metal salt content of the waters, exclusive of the metal bicarbonates. Titration of a separate sample, not previously ion-exchanged by the Amberlite IR-120(H) resin, for alkalinity (methyl orange end point) then gave the metal bicarbonates. The total cation content of the waters corresponded to the summation of the two independent measurements. Total hardness, ammonia nitrogen, chlorides, nitrates, ortho-phosphates, chemical oxygen demand (COD), and methylene blue–active substances (MBAS) were determined using standard procedures (American Public Health Association, 1960).

Process Studies. For the modified Desal process to function satisfactorily during the renovation of the secondary sewage effluents, the resin employed in the alkalization step would need to be able to function efficiently in the bicarbonate cycle and to remove organic matter reversibly from the secondary

Figure 2. Flow diagram of ion exchange process for renovation of secondary sewage effluent

Table II. Accelerated Organic Fouling Test (Amberlite IRA-68)

Bed volume 20 ml.	Temperature 25° C.
Flow rate 16 BV per hour	Regeneration level 110% of theory

	Resin Exchange Capacity, Meq./G.
Fresh resin	6.00
Cycled resin	
1st cycle, 1000 BV	5.90
2nd cycle, 3000 BV	5.92

sewage effluents being treated. Amberlite IRA-68, based on past experiences and studies with regard to the Desal process for treatment of brackish waters, was found to be the only commercially available anion exchange resin ideally suited for this purpose (Kunin, 1965; Kunin and Vassiliou, 1964).

An accelerated organic fouling test was performed to determine how much the anion exchange resin would organically foul when brought repeatedly in contact with sewage water. In the test, approximately 12.7 grams of hydrated resins (41% dry solids) were placed in a 30-ml. sintered glass tube. The resin, approximately 20 ml. in volume, was converted to the HCl form and approximately 20 liters of unfiltered secondary effluent were passed through the resin (upflow) at a linear flow velocity of 16 bed volumes (BV) per hour in a continuous manner. For convenience, the HCl rather than bicarbonate form of the resin was used. Operating the resin in one of the predominant salt forms to which the resin would be converted during the test should not invalidate the results, since the degree of organic fouling should not vary significantly as a function of a particular salt form of resin used in the test. The volume of sewage passed corresponded to roughly 1000 BV. The resin was subsequently regenerated with NH_4OH and the anion exchange capacity of the resin was determined and compared with the anion exchange capacity measured for the fresh resin. The same resin was converted again to the HCl form and another 20-liter quantity of unfiltered secondary sewage water circulated through the resin. This time the 20-liter quantity of sewage effluent was recycled upflow through the resin bed three times (total volume passed $\cong$3000 BV). The secondary sewage water was recycled, since it contained a much larger concentration of potentially fouling organic matter than the ion exchange resin could possibly adsorb. It was therefore felt that it would suffice merely to recycle the solution in order to achieve full saturation of the resin with organic matter. After the treatment, the anion exchange capacity of the resin was again measured (Table II).

Apparently the capacity data show that the resin was not adversely affected by the organic compounds in the secondary sewage effluent; otherwise the capacities of the resins would not have been restored to their original value after regeneration. During regeneration with ammonia, much color, presumably organic in nature, was eluted from the resin. One might expect that with repeated cycling some degree of organic fouling would eventually occur. A precaution that might be taken to minimize this occurrence or avoid it completely would be to subject the resin to a periodic brine
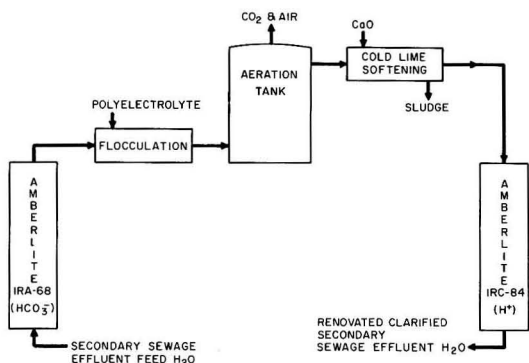
treatment, a practice commonly employed in the ion exchange field to protect anion exchange resins from organic fouling. Primarily because of ion exchange resin regenerant costs, a lime-softening treatment was considered for the dealkalization step of the modified process.

During the development of the final process a series of runs was made using secondary sewage effluent as received. The sewage water contained considerable suspended matter, presumably inorganic in nature, since it contributed very little to the COD. During the upflow alkalization runs an appreciable amount of the coarser suspended matter present in the unfiltered secondary sewage effluent was being retained in the anion exchange resin bed. As a result, clumping problems were experienced, resulting in considerably more channeling than would be expected during upflow operations, and consequently the resin capacity for both inorganic ions and organics was not being efficiently utilized. Because of the entrapment of organic matter in the bed, complete regeneration of the resin could not be realized by employing ammonia at the usual regeneration levels, but could be achieved only when the resin was removed from the column, declumped mechanically by gentle stirring, and subsequently rinsed with a few bed volumes of 10% NaCl solution prior to the ammonia regeneration. To avoid these inconveniences arising because of the relatively small diameter of the ion exchange columns and lines during our laboratory studies, the authors decided to filter the relatively coarse suspended matter from the secondary sewage effluent prior to its passage through the anion exchange resin unit. (Three to four layers of cheesecloth proved to be an excellent filtering medium for this purpose.) In a large scale operation, because of the increased diameters of column and lines, the coarse suspended matter will not significantly reduce the efficiency of the operation and therefore the filtration step can be omitted entirely. By resorting to the filter pretreatment in the laboratory studies, clumping and channeling problems were practically eliminated, the ion exchange resin remained free-flowing during its utilization, and regeneration could be performed in situ using the customary levels of ammonia under gravity flow.

Numerous runs were performed during the development of the final process using prefiltered secondary sewage effluents but, time and time again, fully clarified waters could not be obtained even when lime softening was practiced. Although the soluble inorganic composition of the waters was improved satisfactorily, organic removal, as measured by the COD test, was never as complete as desired. The best removal of organics attained seldom exceeded 50% of the organic matter initially present.

An attempt was made to establish whether or not the lime-softening step was contributing to any degree in reducing the organic content of the aerated anion exchange resin-treated water. Data collected for the alkalized water after aeration and after lime softening for a typical run performed during the early studies are listed in Table III. Based on the COD measurements reported, apparently the bulk of the organics was being removed in the alkalization ion exchange unit and lime softening was contributing little, if any, to reducing the organics further. Though the lime-softened water was of a satisfactory quality as regards its ionic composition, a completely clarified water was not obtained. The treated water had a COD value of 50 p.p.m., hardly suitable for a municipal water supply.

At this point, additional treatment was considered. Based on earlier studies pertaining to the removal of soluble organic matter from aqueous systems (Pollio, 1967), the effectiveness of a bentonite–Primafloc C-7 flocculation treatment was examined as a means of further reducing the organic matter present in the alkalized waters prior to lime softening. An initial flocculation test was consequently performed on a sample of prefiltered secondary sewage to check the feasibility and effectiveness of such a treatment. Results in Table IV refer to data obtained during the flocculation of secondary sewage, not previously treated by the modified process.

A 72% reduction in organic matter (COD) was observed. As would have been expected, the ionic compositional features of the water are not altered to any significant degree. Based on an increase in pH noted after flocculation, the organic materials removed are apparently acidic in nature, as are the MBAS removed.

Optimized Process. The process was subsequently optimized to include the bentonite and Primafloc C-7 treatments as a result of the favorable reduction in organic matter obtained (Table IV). Specific for processing Haddonfield, N. J., secondary sewage effluent waters, the process consisted of: filtration, secondary sewage effluent filtered to remove coarse

Table III. Preliminary Renovation Studies of Haddonfield, N. J., Secondary Sewage Effluents Using Modified Desal Process

	Influent	After Aeration	After Lime Softening
pH	6.95	8.2	8.8
Specific resistance, ohm cm.	1900	2300	2400
Alkalinity, p.p.m. as $CaCO_3$	140	290	230
Hardness, p.p.m. as $CaCO_3$	100	90	45
Cl^-, p.p.m. as $CaCO_3$	55	5	5
Orthophosphates, p.p.m. as $CaCO_3$	22	<1	<1
COD, p.p.m.	90	51	50
MBAS, p.p.m.	0.4	0.2	0.2

Table IV. Flocculation of Haddonfield, N. J., Secondary Sewage Effluent

Dosage levels: 30 p.p.m. bentonite + 10 p.p.m. Primafloc C-7

	Untreated Influent	Flocculated Influent
pH	7.25	7.70
Specific resistance, ohm cm.	1450	1550
Alkalinity, p.p.m. as $CaCO_3$	180	190
Hardness, p.p.m. as $CaCO_3$	100	100
Cl^-, p.p.m. as $CaCO_3$	62	57
NO_3^-, p.p.m. as $CaCO_3$	1.8	1.5
Orthophosphates, p.p.m. as $CaCO_3$	39	33
COD, p.p.m.	162	46
MBAS, p.p.m.	2.0	1.2

sewage particles; alkalization, upflow treatment in pressurized (50-p.s.i.) anion exchange resin (HCO_3^-) unit at a flow rate of 16 BV per hour; flocculation, jar test equipment used [30 p.p.m. of bentonite (as 1% suspension) added at 100 r.p.m.; after 2 minutes 5 p.p.m. of Primafloc C-7 added (as 0.1% product solution); agitation at 100 r.p.m. continued for a total of 5 minutes, then additional 25 minutes at 30 r.p.m.]; aeration, flocculated water aerated for 75 minutes; lime softening, jar test equipment used, a quantity of lime (3.6% suspension) added at 100 r.p.m. equivalent to the total hardness of the sewage water before alkalization (agitation at 100 r.p.m. continued for 5 minutes, then additional 115 minutes at 30 r.p.m.); regeneration, the alkalization ion exchange resin was converted to the free base form employing ammonia as a 1N solution.

A quantity of ammonia corresponding to 150% of the resin theoretical capacity (35 to 36 kilograins per cu. foot) was used initially. Although between 8 and 12 kilograins per cu. foot of resin anion exchange capacity was apparently utilized during subsequent exhaustion cycles employing the Haddonfield, N. J., secondary effluents, regeneration was always performed using the aforementioned quantity of ammonia in order to assure maximum regeneration. This quantity was used because the total anions eluted during regeneration were usually found to be 5 to 8 kilograins per cu. foot greater than the apparent capacity utilized by the inorganic anions. The excess capacity was apparently due to the organic matter adsorbed by the resin. For a 200-ml. resin bed, the regenerant volume was approximately 2½ bed volumes of 1N NH_4OH. Regeneration was performed downflow under gravity at a flow rate of 8 BV per hour. To convert the resin to the bicarbonate form, deionized water, previously saturated with CO_2 at 75 p.s.i., was passed downflow through the resin bed under a 50-p.s.i., CO_2 driving

pressure. Though in actuality an equivalent amount of CO_2 that corresponds to the resin exchange capacity is needed to convert the resin fully to the bicarbonate form, in the laboratory a large excess (30 bed volumes) of carbonated water was used to effect the conversion.

Table V lists alkalization data obtained for bed volume fractions of Haddonfield secondary sewage effluent (Table I) using the optimized process which has been detailed.

During treatment of this particular water, a total of 226 BV of water was processed to a chloride breakthrough of 50%. Analytical data obtained during the further processing—i.e., flocculation, aeration, and lime softening—of 16-BV fractions of alkalized water are listed in Table VI.

Table V. Renovation of Haddonfield, N. J., Secondary Sewage Effluent

(After alkalization)

Bed Volume Fraction	P.P.M. as $CaCO_3$		COD, P.P.M.
	Methyl Orange Alkalinity	Chloride	
1–16	260	0	...
17–32	300	2.5	10
33–48	250	0	...
49–64	270	0	...
65–80	270	0	30
81–96	270	0	...
97–112	270	5	...
113–128	270	5	33
129–144	270	10	...
145–160	260	15	...
161–176	260	20	35
177–192	260	22.5	38
193–208	255	17.5	...
209–226	255	22.5	39

Table VI. Renovated Haddonfield, N. J., Secondary Sewage Effluent

(After alkalization, flocculation, aeration, and lime softening)

Bed Volume Fraction	pH	Specific Resistance, Ohm Cm.	C.O.D., P.P.M.	MBAS, P.P.M.	Hardness, P.P.M.	Ortho-phosphates, as $CaCO_3$	NO_3^-	Cl^-
1–16	9.0	3600	13	0.3	30	<1	0.8	0
17–32	9.0	3000	18	0.3	30	<1	0.8	2.5
33–48	9.0	3300	18	0.3	30	<1	0.8	0
49–64	9.0	2700	17	0.3	40	<1	0.8	0
65–80	8.9	2600	17	0.3	42	<1	0.8	0
81–96	9.0	2600	20	0.3	45	<1	0.8	0
97–112	9.0	2800	17	0.3	43	<1	0.8	5
113–128	8.9	2500	26	0.3	44	<1	0.8	5
129–144	8.9	2600	29	0.3	46	<1	0.8	10
145–160	9.0	3600	26	0.3	30	<1	0.8	15
161–176	9.0	2800	29	0.3	42	<1	0.8	20
177–192	8.9	2600	26	0.3	44	<1	0.8	22.5
193–208	9.1	3000	17	0.3	36	<1	0.8	17.5
209–226	9.0	2500	21	0.3	48	<1	0.8	22.5

Table VII. Dealkalization of Modified Desal Processed Secondary Effluent Using Amberlite IRC-84

Resin bed volume. 25 ml.
Exhaustion flow rate. 16 BV per hour

Bed Volume Fraction	pH	Specific Resistance, Ohm Cm.	C.O.D., P.P.M.	Hardness, P.P.M.	NH_4^+, as $CaCO_3$	NH_4^+, P.P.M. As Is
1–16	3.6	100,000	15	<1	0	0
17–32	3.5	90,000	...	<1	0	0
33–48	3.5	13,000	...	<1	<1	<1
49–64	3.7	13,000	17	<1	3	1.1
65–80	3.9	21,000	...	<1	3	1.1
81–96	4.0	19,000	...	<1	3	1.1
97–112	4.5	18,500	17	<1	3	1.1
113–128	5.2	17,000	...	<1	5	1.8
129–144	5.6	15,000	...	<1	8	2.9
145–160	6.0	11,200	...	<1	10	3.6
161–176	6.1	9,300	18	<1	14	5.0
Influent	9.0	2,900	21	40	50	18

Greater sedimentation and clarification rates are obtained after lime softening if the sludge from the flocculation and aeration treatment is partially retained in the system prior to lime treatment. The sludge apparently acts as a substrate or nucleating agent for the lime during the lime-softening step and consequently improved sedimentation rates are observed because of the increased sludge density.

After treatment no ammonia (or ammonium ions) was removed. Its removal and further purification of the sewage effluent were achieved by dealkalizing the waters through a column of Amberlite IRC-84 operated in the hydrogen cycle. The cation exchange unit also removed any sodium and potassium salts that remained solubilized after the lime-softening treatment.

Data obtained during processing of the 226-BV composite water using the weak cation exchange resin are presented in Table VII. COD values approach those measured for Philadelphia city water (10 to 15 p.p.m.). The effluents from the dealkalization unit are rich in CO_2, which contributes to lowering the pH of the effluents. To minimize corrosion problems, the effluents would be aerated initially to expel most of the free CO_2. Since full deionization of the sewage effluent is not required, all of the water need not be treated by the cation exchange unit; the fraction treated need be only that required to reduce the salt content to that of the normal water supply of the community. This mode of operation will further lower the over-all costs. The normal ion exchange water treatment practice of split-stream operation would then be practiced by blending a portion of the influent stream to the dealkalization unit with the aerated dealkalized effluent to produce a desired pH. The split-stream operation will not increase the total dissolved solids significantly. In fact, a treated effluent with some mineral content would be more desirable than a completely deionized water.

Table VIII summarizes the processing data obtained during the renovation of the Haddonfield, N. J., secondary sewage effluent (226 BV) using the optimized process with and without the dealkalization step. In addition, the chemical composition of the renovated waters is compared with the chemical composition of the secondary effluent before undergoing tertiary treatment.

Cost Estimate. The operating costs of the secondary sewage renovation process based on the optimized modified process were calculated for plant sizes of 1,000,000 and 10,000,000 gallons per day, on the basis of results obtained during

Table VIII. Renovation of Haddonfield, N. J., Sewage Effluent

	Secondary Effluent (before Tertiary Treatment	Tertiary Effluent	
		Not dealkalized	Dealkalized
pH	7.8	9.0	4.5
Specific resistance, ohm cm.	1700	2900	29,700
COD, p.p.m.	90	21	17
MBAS, p.p.m.	2	0.3	0.3
Hardness, p.p.m. as $CaCO_3$	98	40	<1
NH_4, p.p.m. as $CaCO_3$	50	50	<5
Total alkalinity, p.p.m. as $CaCO_3$	160	220	10
Cl^-, p.p.m. as $CaCO_3$	45	22.5	22.5
NO_3^-, p.p.m. as $CaCO_3$	1.5	0.8	0.8
Orthophosphates, p.p.m. as $CaCO_3$	33	<1	<1

treatment of the Haddonfield, N. J., secondary effluent water. The authors assumed that CO_2 would be readily available from the flue gases resulting from the combustion of the gases emitted from the secondary treatment digesters and therefore only equipment costs for compressing the flue gas, etc., are included in the total costs. Capital investment (including resin costs) for the 1,000,000- and 10,000,000-gallon per day installations were approximated to be, respectively, $173,000 and $1,400,000.

In Table IX the costs have been itemized for the various stages of the discussed optimized process. The costs include both equipment and chemical costs, equipment being amortized over 10 years and the resin over 3 years. In the flocculation step calculations, it was assumed that the lime-softening equipment would be used. With regard to ion exchange resin life, it should be realized that a secondary sewage effluent, in terms of ion exchange resins, is less aggressive than many of the surface water supplies and sugar liquors customarily processed by ion exchange resins. Though no extensive resin life study has been made, it is suspected that the amortization time of 3 years used in the calculations for expected resin life may be a conservative figure.

Since the total dissolved ionic contents of secondary sewage effluents are usually much lower than those found in brackish waters, regeneration costs of the ion exchange units used in the alkalization and dealkalization steps are correspondingly less than those encountered when weak electrolyte ion exchange resins are used to process brackish waters.

Discussion

The modified Desal process for the renovation of secondary sewage effluents appears to offer a significant advance in processing sewage effluent waters to render them useful for industrial, agricultural, or domestic use. The modified process for sewage water renovation appears to go a step beyond the proposed activated carbon–type tertiary treatment processes, since it brings about simultaneous reduction in both the organic and inorganic mineral contents of the sewage water. During prolonged exposure tests (3 months), processed sewage effluents, with or without additional treatment with the cation exchange resin for ammonium removal, have shown no visual evidence of algae growth. Turbidity was absent, no odor was detectable, and no significant compositional changes have been noted. The problem of pathogens was not investigated. However, there is evidence that chlorination (Morris and Weber, 1962) and lime softening (Thayer and Sproul, 1966) do eliminate certain bacterial virus from water during processing.

The process offers much flexibility, since it may be engineered to produce a water for a variety of uses. Where partially processed water is the goal, such that its dissolved ionic and organic contents have been lowered to acceptable levels for direct discharge into streams or waterways, the process possibly could be operated without the flocculation and lime-softening steps; for industrial use, the waters may be sufficiently processed without the added dealkalization step, especially if the secondary treatment (biological) is producing a nitrified effluent. If the sewage plant has not been operated in such a manner, the dealkalization step is required to remove ammonium ions which might prove objectionable.

Presupposing that a cheap source of CO_2 were not available, the economics of operating this modified process would be

Table IX. Cost Estimate for Renovation of Haddonfield, N. J., Secondary Sewage Effluent

	$ Cost/1000 Gal.	
	1,000,000 gal./day	10,000,000 gal./day
Alkalization	0.0655	0.0631
Dealkalization	0.0500	0.0478
Carbonation	0.0030	0.0030
Degasification	0.0042	0.0029
Flocculation (chemicals only)	0.0436	0.0436
Lime softening	0.0158	0.0158
Grand total	$0.1821	$0.1762

considerably higher, since recovery of CO_2 is not practical. Fortunately, however, availability of CO_2 should not be a problem, especially in sewage plants which practice secondary treatment. Since the flue gases from the digesters are rich in CO_2, they may be used directly, after being pressurized, to convert the anion exchange resin (alkalization step) to the bicarbonate form.

In instances where the renovated water will be recycled and renovated more than once, there will be a gradual buildup in ionic solids. During each renovation, if the dealkalization step is not incorporated into the process, sodium ions tend to accumulate if not removed. This situation can be avoided by dealkalizing the waters totally or partially every other cycle or two, depending on the extent of the sodium ion buildup and the required end use for the renovated water.

Disposal of waste regenerant from the ion exchange units and sludge from the flocculation and lime-softening treatments should present no problem. These could be readily combined with the solid waste from secondary treatment and disposed of using the normal practice of the sewage treatment plant.

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Organic Content of Southwest and Pacific Coast Municipal Waters

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■ Water samples from municipal supplies in some Southwest and Pacific Coast communities were analyzed for organic content by a pyrographic technique. The organic content averaged 0.9 mg. of carbon per liter for the supplies from underground sources. Municipal supplies obtained from surface sources in desert and semiarid regions had organic contents from 1.1 to 2.7 mg. of carbon per liter. Those procured from surface waters in the northern Pacific Coast, which has abundant rainfall and heavily forested drainage basins, had organic contents from 3.7 to 7.7 mg. of carbon per liter.

A study was undertaken to accumulate data on the organic content of water available to consumers through municipal distribution systems, and to assess three factors which could affect the organic content—i.e., source, climates, and treatment. The only information found in the literature was that the carbon chloroform extract (CCE) should not exceed 200 μg. per liter in municipal waters, clean surface and ground waters usually contain only 25 to 50 μg. per liter of CCE, and highly colored waters may exceed this level (American Public Health Association, 1965).

For this study, municipal supplies from communities in the Southwest and Pacific Coast regions of the United States were used. In these regions, the climate ranges from desert to rain forest with the accompanying changes in vegetation. The sources are both surface and underground waters, and the treatment before delivery to the consumer varies from only chlorination to complex processes using coagulation, filtration, and chlorination (U.S. Public Health Service, 1964).

Experimental

Apparatus. A detailed description of the apparatus used for the pyrographic measurement of the organic content of water is presented by Lysyj and Nelson (1967). The apparatus consists of a steam generator and a sample injection system connected to a pyrolysis chamber contained in a micro-combustion furnace. This chamber is in turn connected to a flow stabilization column of glass beads installed in a gas chromatograph which is equipped with a hydrogen flame ionization detector. A 1-mv. recorder with a 2-inch-per-minute chart speed completes the apparatus.

Procedure. Sample bottles cleaned with hot nitric acid containing 10% sulfuric acid were used for sample collection. The water samples were collected from the tap in each community listed in Tables I and II.

In the analysis, a 0.25-ml. aliquot of a water sample was injected into the pyrolysis chamber at 6-minute intervals. The fragments, which were produced by the pyrolysis of the organic matter present in the water, were transported by the steam carrier gas through the flow stabilization column to the detector. Because no separation is achieved on this column, the total organic fragments were measured by the flame ionization detector. The organic content of the water sample was calculated from the average peak area. Materials representative of the major organic classes present in the water were used for calibration.

Table I. Organic Content of Municipal Waters from Ground Sources

Municipality	Organic Content, Mg. Carbon/Liter
Arizona	
Flagstaff	0.7
Grand Canyon	0.8
Kingman	1.6
California	
Carlsbad	0.8
Paso Robles	0.9
Salinas	0.9
San Juan Capistrano	1.5
Santa Ana	0.7
Santa Barbara	1.0
Thousand Oaks	0.9
New Mexico	
Albuquerque	0.9
Grants	0.7

Table II. Organic Matter in Waters Distributed by Municipalities Utilizing Surface Sources

Municipality	Source	Organic Content, Mg. Carbon/ Liter
Arizona		
Williams	Surface	1.3
California		
Alameda	Reservoir	2.1
Del Mar	Cottonwood Creek and Otay River	1.1
Los Angeles	Owens River	2.7
Redding	Sacramento River	4.8
San Diego	Cottonwood Creek and Otay River	1.4
San Luis Obispo	Salinas River and Creek	1.3
San Mateo	Lakes and Streams	1.1
Santa Rosa	Russian River	3.7
Santee	Cuyamaca Lake	1.6
Ventura	Ventura River	2.5
Nevada		
Las Vegas	Lake Mead	1.3
Reno	Truckee River and Hunter Creek	1.6
New Mexico		
Santa Fe	Santa Fe River	1.3
Oregon		
Eugene	McKenzie River	7.7
Gold Beach	Rogue River	6.3
Medford	Big Butte Springs and Bear Creek	4.7
Portland	Bull Run Lake and Bull Run River	7.7
Seal Rock	Deer Creek	3.9
Tillamook	Killiam and Fawcett Creeks	6.4

Results and Discussion

The organic contents of the municipal water supplies originating from ground waters are presented in Table I. These municipalities are located in southern California and the Southwest, and all use wells as the source of water with the exception of the Grand Canyon which uses an infiltration gallery. In general, these waters, if treated, are only chlorinated before use. Table I shows these municipal water supplies averaged 0.9 mg. of carbon per liter with a range of 0.7 to 1.6 mg. of carbon per liter, which indicates that a water supply obtained from underground sources in a region with a low annual rainfall and sparse vegetation would have an organic content of about 1 mg. of carbon per liter. No data on organic contents are available for well waters from northern California or Oregon where the precipitation is greater and the land is heavily forested.

Organic contents are presented in Table II for the supplies in municipalities utilizing surface waters as a source. The treatment of these waters before distribution to the consumer varies from only chlorination to a complete purification treatment including coagulation and filtration. There was no correlation between the amount of organic matter and the treatment given the water. Municipal supplies obtained from surface sources generally have much higher organic contents than those procured underground (Table II). The municipalities in Oregon and northern California have waters with high organic contents as indicated by values ranging from 3.7 mg. of carbon per liter for Santa Rosa, Calif., to 7.7 mg. of carbon per liter for Portland and Eugene, Ore. These high values are the result of climate and vegetation. The northern Pacific Coast region has a high rainfall, and the drainage basins are heavily forested which contributes very significantly to the organic content of the water. For example, the source of water for Portland is a protected, uninhabited mountainous watershed on the Cascade mountains and is densely covered with trees and other vegetation. The organic matter in this municipal water is derived solely from vegetation with none originating from pollution.

In contrast, municipal waters procured from streams in the desert or semiarid Southwest region with sparse vegetation have a much lower organic content. The level of organics in the streams approaches that of the ground waters in the area as indicated by a comparison of the two nearby municipalities of Santa Fe and Albuquerque. The organic content of Santa Fe water obtained from the Santa Fe River was 1.3 mg. of carbon per liter and that of Albuquerque water from wells was 0.9 mg. of carbon per liter. Similarly, waters procured from ground and surface sources in the adjacent communities of Flagstaff and Williams had organic contents of 0.7 and 1.3 mg. of carbon per liter, respectively.

The organic contents of all these municipal waters are in the range of values for natural waters reported by other investigators using various analytical techniques. In a study of 529 lakes, the organic carbon content ranged from 1.2 to 28.5 mg. of carbon per liter with a mean of 7.7 mg. of carbon per liter (Birge and Juday, 1934). Of these lakes, 327 had an organic content between 3 and 10 mg. of carbon per liter. Other investigators found lake and reservoir waters contained from 1.7 to 15.2 mg. of carbon per liter (Datsko, Vasil'eva, et al., 1964; Krylova and Skopintsev, 1959; Votintsev, 1955). River waters had from 2.0 to 34.8 mg. of carbon per liter depending on the season (Alekin and Brozhnikova, 1960; Datsko and Vasil'eva, 1961; Krylova and Skopintsev, 1959).

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BOOKSHELF

New book takes an old look at industrial hygiene and toxicology

Analytical Toxicology of Industrial Inorganic Poisons. Morris B. Jacobs. xxv +943 pages. John Wiley & Sons, Inc., New York, N.Y. 10016. 1967. $25, hard cover. *Herbert E. Stokinger is chief, Laboratory of Toxicology and Pathology, and Robert G. Keenan is associate chief, Occupational Health Program, of the National Center for Urban and Industrial Health, Cincinnati, Ohio 45202*

By Herbert E. Stokinger and Robert G. Keenan

This volume is an enlarged edition of M. B. Jacobs' *Analytical Chemistry of Industrial Poisons, Hazards, and Solvents,* which appeared in 1949, but which now is confined solely to inorganic industrial chemicals.

The title is unfortunate in two respects. First, the word "poison" is archaic, having been abandoned by toxicologists and industrial hygienists alike for several years—industry is no longer to be regarded as a producer of poisons. Second, "analytical toxicology" is a meaningless phrase. A more descriptive title would have been *Analytic Chemistry, Toxicology, and Industrial Hygiene of Industrial Inorganic Chemicals.*

As the title should have indicated, the book is a composite of analytic methods useful in industrial hygiene (and air pollution) and the toxicology and industrial hygiene of commercial chemicals. The part concerned with analytic methods far excels the portion on toxicology and industrial hygiene, for the late author was preeminently an analytic chemist and only secondarily a toxicologist and industrial hygienist.

The analytic chemistry sections of this book contain many well-prepared procedures, including some of the best from the older literature. We were disappointed, however, to find the procedures limited almost exclusively to colorimetric and gravimetric methods

of analysis. For example, in the entire book, the author has cited but three emission spectrographic methods, of which only one was published in the past 20 years. Hence, no recognition is given to the increased specificity, sensitivity, precision, and accuracy now realized with a host of physical and combined chemical-physical methods of analysis which have become available since the publication of Dr. Jacobs' previous text on this subject.

Omissions

Other methods and techniques are notably absent. For example, there is no citation of the microprocedures for the colorimetric determination of free silica or of the diffusion methods for the separation of fluorides. Also, there is no mention of the highly refined fluorometric methods for beryllium, which provide reported sensitivities of determination 10 to 100 times that of the procedure presented in Chapter X. Such methods have assumed great importance in recent years because of the increased emphasis on the analysis of body tissues and fluids and of personal environmental samples for trace quantities of agents.

It is regrettable that Dr. Jacobs did not see fit to include the latest analytic techniques along with the best of the older methods. With the current recognition of the importance of characterizing and determining all of the chemical agents in samples representing mixed environmental exposures and in biologic samples, many of us are taking advantage of ion exchange and gas chromatography combined with well-refined spectroscopic methods of analysis (emission, mass, infrared, ultraviolet, visible, and atomic absorption) in solving the complex analytic problems which we face routinely. Hence, such procedures should have been highlighted in this widely used text for industrial hygiene chemists,

because the book is unsurpassed in providing detailed procedures for the analysis of the commonly encountered inorganic chemicals.

Outdated references

In its toxicologic and industrial hygiene coverage, the volume is rather elementary and suffers again in many important sections from lack of up-to-date references. For example, in the section dealing with halogenated compounds, only 4 of 56 references are dated since 1949. The following section contains only 3 of 88. However, the section on clinical chemistry and industrial toxicology fares better, containing 92 of 142 references dated since 1949.

Possibly because of the author's failure to update the volume, there are several inaccuracies regarding the acceptable air standards for industry—many of those quoted are either out of date or nonexistent. So slight is the updating of this book that it represents, with few exceptions, more closely a reprinting than a revised edition.

One man's view of industrial water pollution control

Industrial Water Pollution Control. W. Wesley Eckenfelder, Jr. vii + 275 pages. McGraw-Hill Book Co., Inc., New York, N.Y. 10036. 1966. $14.50, hard cover. *Ross E. McKinney is Parker Professor of Civil Engineering, University of Kansas, Lawrence, Kan. 66045*

By Ross E. McKinney

Professor W. Wesley Eckenfelder, Jr.'s new book on industrial waste pollution control is a very ambitious undertaking. As stated in the preface, the

automated colorimetric analysis of SO$_2$ NO$_2$

Waco's Air Analyzer is truly a continuous sampling colorimeter, automating the accepted chemical methods of analysis for sulfur dioxide and nitrogen dioxide providing: *reliability* . . . highest quality components used throughout. Designed for continuous operation with *flexibility* . . . convert from SO$_2$ to NO$_2$ in 20 minutes. Variable range, from 1 to 8 ppm full scale. *Accuracy* . . . zero drift. Less than ±3% in 7 day periods. Automatic zero and photometer calibration every 24 hours.

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aim of this book is to establish a basic approach to industrial waste evaluations rather than to present detailed data on specific industrial wastes. This approach, no doubt, has considerable merit.

Many years of experience in solving industrial waste problems have given Professor Eckenfelder a valuable insight into this vital area of pollution control. Over the years he has helped organize and teach the Summer Institute in Water Pollution Control at Manhattan College. These two facts together with his regular teaching experience combine to make Eckenfelder a perfect author for a basic text in industrial wastes. The notes developed form the basis for this book.

Unfortunately, because of Eckenfelder's extensive background, there is a tendency to expect his book to be all-inclusive. However, no one text can hope to cover all topics related to industrial wastes in sufficient depth to satisfy all readers. The author has indicated that his book is intended for the first year graduate student in civil engineering and for practicing engineers.

Inadequate background

This book contains much valuable information; but it should be used with caution. It is definitely not a book for the inexperienced young engineer desiring an insight into industrial waste problems or for the engineering student without the assistance of a teacher with considerable industrial waste experience. There are simply too many broad statements and precise equations presented without adequate background development or references.

The problem that the author faced was to expand a basic set of notes into a full book without making the final product too large, but he appears to have fallen short of the optimum results. It may well have been a case of too much familiarity with the subject and not enough familiarity with the reader's ability to bridge the gaps. In any event, the final product is still little more than a series of notes and problems definitely lacking sufficient explanations.

Specifically, this book consists of one chapter on "Source and Characteristics of Industrial Wastes" and 19 chapters on different waste treatment processes and concepts. Unfortu-

nately, Eckenfelder did not choose to discuss the philosophy of industrial waste control. One of the prime problems lies in the proper understanding of the social, political, and economic relationships of industrial wastes, and any book dealing with industrial wastes which ignores these vital topics must be considered as inadequate.

Basic approach

The basic approach to industrial waste control lies in evaluating waste quantities and their characteristics, reducing wastes to a minimum through in-plant changes and improved housekeeping, evaluating effluent requirements, and determining the optimum treatment system to produce the desired results. Unfortunately, Eckenfelder devoted little time to the first three parts of this problem. By passing them in a few brief pages, the impression is given that these items are not really important. Actually, very little consideration was given to the last part of this problem. In effect, Eckenfelder chose to look at discrete processes used in industrial waste treatment and ignored the crucial role of tying the various unit processes together into a complete industrial waste treatment system.

False impression

Further examination of specific sections of this book indicates that Eckenfelder has chosen to ignore opinions which disagree with his views. The net result of this technique is to give the reader the impression that there are no disagreements with the opinions stated in this book. But improvement in treatment processes and improved understanding of basic concepts can come only through competent discussion of different concepts and presentation of sufficient data to allow the reader to draw his own conclusions.

This deficiency is most apparent in the area of biological treatment. Too little information is presented for any rational understanding of the various biological treatment processes. It is also regrettable that there was not better development of the various design factors in the design examples. In their present form the design examples leave much to be desired and may well lead to serious problems if they are not carefully understood.

Overall, Eckenfelder's book presents little new information that has not already appeared in other books (including his own) on the general concepts of waste water treatment. In spite of its faults, the volume will prove of some value to the experienced engineer who wants a quick review of the various waste water treatment processes, whether for domestic sewage or industrial wastes.

Index to Catalog of Information on Water Data-Surface Water Stations Reported by Federal Agencies. Compiled by J. R. Rapp, W. W. Doyel, and K. F. Harris. xxii + 517 pages. U.S. Geological Survey, Washington, D.C. 20242. 1966. Free on request, paper.

More than 20,000 stations throughout the U.S. are collecting surface water data at regular intervals. These stations supply data on the amount of

water passing through rivers, lakes, reservoirs, and estuaries.

The catalog contains information pertaining to the location of the stations, the reporting agencies, and the type of data available such as stage, discharge, low flow, high flow, drainage area, flood duration, flood frequency, means and extremes of flow, and runoff. Although the catalog does not contain the actual data, it serves as a guide to the location of the data.

The catalog is one of four sections which make up the "Catalog of Information on Water Data," a coordinating source for the collection of water data by federal agencies, and will aid in the design and operation of a national water data network to solve the problems of water supply, water quality, and water development and management.

Index to Catalog of Information on Water Data-Water Quality Stations Reported by Federal Agencies. Compiled by K. F. Harris, J. R. Rapp, and W. Doyel. xxii + 151 pages. U.S. Geological Survey, Washington, D.C. 20242. 1966. Free on request, paper.

More than 6000 stations throughout the U.S. are collecting water quality data at regular intervals. These stations supply data on water quality of streams, lakes, estuaries, and ground waters.

The catalog contains information pertaining to the location of the stations, the reporting agencies, the frequency of reporting, and the type of data available such as physical, chemical, organic, biological, and information on sediment. The catalog serves as a guide to the location of the data and is one of four sections which make up the "Catalog of Information on Water Data."

Highways and Environmental Quality. Highway Research Record No. 182. 38 pages. Highway Research Board, Washington, D.C. 20418. 1967. $1.60, paper.

Treatment and Disposal of Wastes. World Health Organization Technical Report Series No. 367. 30 pages. World Health Organization, Geneva, Switz. 1967. 60 cents, paper.

Study of Strip and Surface Mining in Appalachia. 78 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1966. $1.00, paper.

Managing the Air Resource in Northeastern Illinois. Technical Report No. 6. xvii + 112 pages. Northeastern Illinois Planning Commission, Chicago, Ill. 60606. 1967. $5.00, paper.

Proceedings: The Third National Conference on Air Pollution. Public Health Service Publication No. 1649. xvi + 667 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1967. $4.25, paper.

NEW PRODUCTS DIGEST

Bimetal Thermometer

The Multiform bimetal, adjustable (5-inch) dial, stainless steel thermometer features a silicone-dampened moisture- and fume-proof mechanism and a cupped scale to reduce parallax. Accurate within 1% of range, the thermometer can be adjusted externally. Princo Precision Thermometer and Instrument Co.   **64**

Proportioning Pump

Model 67-JP proportioning pump feeds and regulates the flow of liquid fertilizers, herbicides, pesticides, or fumigants in sprinkler or irrigation water. Metering accuracy with the pump is said to be ±0.5%. Inject-O-Meter Manufacturing Co.   **65**

Cooling Tower Treatment Chemicals

Zimmite series 500 water treatment chemicals for cooling tower treatment are based on chelating agent complexes rather than conventional phosphate sequestering agents. Overtreatment leads to faster removal of old deposits rather than new scale formation, the company notes. Zimmite B-530, a single premium product in the series, treats for mud, scale, rust, algae, and slime. W. E. Zimmie, Inc.   **66**

Fine-Particle Dust Collector

The twin cyclone dust collector is 85–95% effective in collecting particulates in the 4 to 15μ range—coal dust, bark char, phosphate dust, salt cake, and other industrial dusts, according to the company. Other features attributed to the device are low erosion and plugging incidence, minimal cross-hopper flow, and a wide range of loadings (0.25 to 20.0 grains per standard cu. ft.). The company also notes that collection efficiency is independent of inlet dust loading. Combustion Engineering, Inc.   **67**
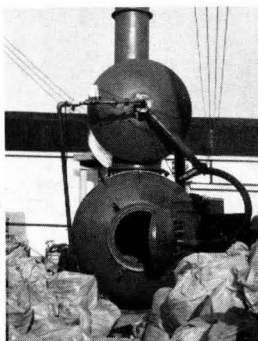
Midland-Ross Corp.

Genera Tire & Rubber Co.
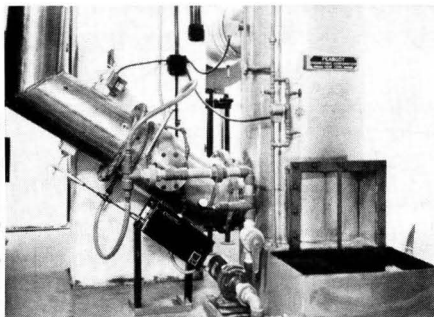
Peabody Engineering Corp.

Point-of-use pollution control devices

A compact, automatic, commercial industrial incinerator (top, left) accepts a wide variety of refuse without presegregation. Dual-chamber configuration allows refuse combustion (lower cylinder) and afterburner consumption of smoke, gases, and fumes (upper cylinder). The company claims that only heated air is discharged from the stack. Midland-Ross Corp.   **61**

A portable sewage treatment system (top, right) can process as much as 10,000 gallons of raw sewage daily. Designed for facilities such as military camps, ships, or recreational areas, the unit operates as follows: Raw sewage enters a holding tank where it is ground, screened, then sprayed over a bed of microorganisms before being released, for up to 85% BOD reduction. General Tire & Rubber Co.   **62**

A packaged gas-washing unit (bottom) cycles hot, dirty gas from incinerator operations through a quench spray which removes large particulates. The gas is then restricted by an adjustable damper plate and discharged through a flue. Completely automatic, the unit meets New York City's pollution control codes, Peabody Engineering Corp.   **63**

Pesticide Analyzer

A dual-channel isothermal gas chromatograph determines chlorinated pesticides to the picogram level and phosphorylated pesticides to the $1/10$ nanogram level. The unit incorporates both an electron capture and a sodium thermionic detector, enabling simultaneous assay of these pesticides. Trace amounts of other chlorinated organic compounds or organophosphates can also be detected. Packard Instrument Co., Inc.   **68**

Dual-Purpose Coagulant

A combination primary coagulant and coagulant aid eliminates the need for separate treatment steps for small to medium size plants. The liquid promotes faster settling floc formation and even removes oil from waste water, the company notes. At high dosages, the material serves as a demulsifier. It is available in 30- or 55-gallon drums. W. R. Grace & Co.   **69**
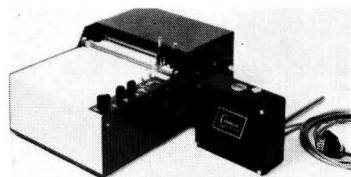
Protein and Nucleotide Detector

An ultraviolet flow analyzer features an automatic scale expansion device for use in measuring trace quantities of proteins and nucleotides. Sensitivity is automatically switched between two ranges to give maximum scale magnification and prevent the pen from running off-scale when strong absorbers are measured. Two styles of 8-inch wide preprinted chart paper (transmittance units or absorbance units) are available. Single or dual cuvette capacity may be selected, with dual phototube detectors in each to provide automatic compensation for source lamp brightness fluctuations. Model 1205 fraction collector provides plug-in connection with the flow analyzer, and collects up to 60 samples (at preset intervals with a timing accessory) from up to four sources (240 fraction capacity). Canal Industrial Corp.   **70**
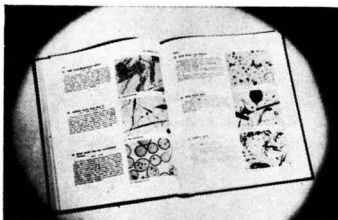
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Standard Spectroscopy Solutions

Standard solutions having ion concentration levels of 1000 p.p.m. are available for the 12 commonly analyzed elements: Ca, Cr, Co, Cu, Fe, Pb, Mn, Ni, K, Ag, Na, and Zn. Beckman Instruments, Inc.   **71**

Water and Waste Analysis Kit

A rugged photometer, a procedure handbook (with calibrations) for all popular water and waste tests, and all necessary reagents and labware for 14 standard tests, are packaged in a waterproof, chemical-resistant, battery or line-operated, compact case. Tests included are for ammonia, chlorine, fluoride, iron, nitrate, nitrite, pH, phosphate, polyphosphate, silica, sulfate, sulfite, and turbidity. Optional extra tests are for amines, aluminum, bromine, chromium, color of water, copper, cyanide, dissolved oxygen, hydrazine, manganese, phenols, silver, surfactants, tannin and lignin, and zinc. Delta Scientific Corp.   **72**
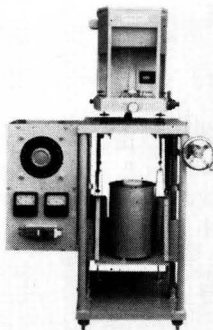
Direct-Reading Thermal Balance

Changes of mass within the range −10 mg. to +120 mg. can be continuously weighed and observed without manipulation of balance controls of this direct-reading thermal balance. If the reading goes off-scale, it can be brought back on-scale by turning a knob. The balances are available in capacities of either 100 or 200 g. with readability of 0.1 mg., and a choice of iron-chromium-aluminum heaters which operate to 1000° C. or silicon carbide heaters which operate to 1500° C. Voland Corp.   **73**
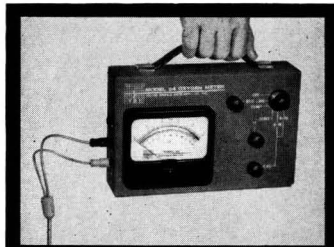
is this the answer to your dissolved O₂ problem?
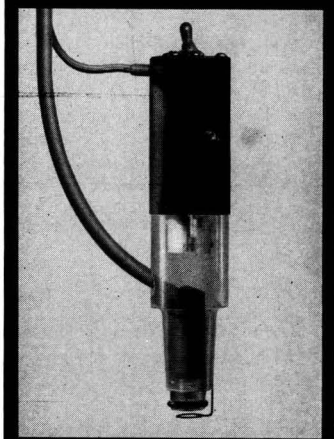
The new YSI Model 54 answers the need for a quickly calibrated, temperature compensated instrument with recorder output for accurate single measurements or short-term monitoring of dissolved oxygen. It reads and records directly in ppm. The extremely compact Model 54 is ideal for both lab use and field sampling of sewage plants, lakes, rivers, etc. to 50 feet (100 feet on special order). A unique, self-agitating motorized accessory probe permits BOD bottle readings in less than a minute without a stirrer. Instrument and probe under $500.00. Write for bulletin.

NEW LITERATURE DIGEST

Fabric filters. The series 800 fabric filter collectors for cleaning 2000 to 300,000 c.f.m. of gas are illustrated in bulletin 910. The bulletin describes mechanical-shake type filters, which are available in 15 sizes with cloth area from 1600 to 12,800 sq. ft. Research-Cottrell, Inc. **95**

Thermoplastics. An 8-page brochure highlights the special characteristics of Kralastic ABS thermoplastics, a light-weight, noncorrosive, heat-resistant, rigid plastic that can absorb sudden sharp impacts without shattering. Uni-royal, Inc. **96**

Industrial desalination systems. Bulletin BW-1/867 describes the BW series conversion system, which reduces dissolved solids in brackish or problem water by reverse osmosis. The system is self-contained and requires only electrical power for operation. Tubular desalting modules offer flexibility. Universal Water Corp. **97**

Deaerating heater. A 6-page bulletin describes the SSC deaerating heater, which is a small, simple, compact unit for use in smaller steam generating plants, according to the company. The special heater reduces corrosion and pitting in boilers and condensate return lines, improves thermal efficiency, and provides maximum storage for condensate surge, the company adds. Graver Water Conditioning Co. **98**

Supplies for testing pH. A 16-page bulletin provides reference tables for selecting and ordering equipment supplies for pH meters, and selecting proper buffer standards for pH measurement. Information for ordering electrodes—including glass, reference, and combination and metallic electrodes—is provided. Beckman Instruments, Inc. **99**

Torque-flow pumps. Bulletin P10-B65 discusses the features of the model E torque-flow pumps designed for liquid and solids handling. Features include heads more than 200 feet, 4000 g.p.m. capacity, and 57% efficiency. Arthur G. McKee & Co. **100**

Heat exchanger. Catalog 102 describes the Holo-flite processor, an indirect heat exchanger-conveyor. Heat is transferred to or from the heat exchange agent through the surfaces of the hollow flights and helical shafts. Heating, cooling, drying and calcining, and solvent recovery may be accomplished with the device. Joy Manufacturing Co. **101**

Membrane filtration procedures. A new 56-page manual details membrane filter techniques for making bacteriological and microbiological examinations. The handbook includes routine bacteriological examination of dairy products, examination of beer and brewery operations, clinical membrane bacteriology, and other specialized chapters. Gelman Instrument Co. **102**

Desiccant dryers. Bulletin HB-326 describes the type HB pneumatic Heat-Les desiccant dryers with optional electrical control. The dryers feature

adjustable purge rate, a repressurizing device to prevent desiccant breakup and downstream line surges, separate desiccant drain and fill ports, and explosion-proof construction, the company notes. Pall Corp. **103**

Dew point transducer. Models 016-30, -31, -32, and -33 dew point transducers are presented in a fact sheet. These thermoelectric hygrometers feature modularized solid state plug-in circuitry, choice of field or laboratory configurations, and either analog or digital outputs. Climet Instruments, Inc. **104**

Dehydration process. A continuous sludge dehydration process, described in an illustrated 4-page folder, can be adapted to a number of waste drying problems, including disposal of garbage and industrial wastes, rendering organic products, paper and pulp wastes, and milk whey. The resultant dried sludge is sterile. Fred S. Carver, Inc. **105**

Pollution pamphlets. Two public interest pamphlets, "Don't Burn Those Leaves!" and "Polluted Air: The Black Cloud That Covers Our Metropolis," are available from the Air Pollution Control Division, St. Louis County Health Department, 801 S. Brentwood Blvd., Clayton, Mo. 63105. (Write direct.)

Ultrasonic energy breaks chemical bonds in coal derivatives. Neat, coal-derivative compounds such as tetralin, 1-methylnaphthalene, and pyridine undergo chemical reactions upon exposure to ultrasonic energy and produce low molecular weight compounds in the process. Low molecular weight compounds obtained by sonolysis include ethylene, hydrocyanic acid, methane, hydrogen, carbon monoxide, and carbon dioxide, depending on the experimental conditions. Under certain conditions tetralin yields diacetylene.

All experiments were conducted in the absence of water and employed a commercial ultrasonic generator operating at a frequency of 80 kc. with a total output of 80 watts. Bureau of Mines Report of Investigations 7027 entitled "Chemical Reactions Produced by Exposing Coal Derivatives to Ultrasonic Energy," by Theodore Kessler, A. G. Sharkey, Jr., and R. A. Friedel, October 1967. (Write direct.)

Program for the 1968 Gordon Research Conference

ENVIRONMENTAL SCIENCES AND ENGINEERING—WATER

June 10–14, 1968
New Hampton School, New Hampton, N. H.

Chairman: Walter J. Weber, Jr., Univ. of Michigan

Vice-Chairman: August T. Rossano, Jr., Univ. of Washington

SURFACE PHENOMENA IN AQUEOUS SYSTEMS

Monday: 1. Sorption at the Solid–Water Interface

Session 1.1 (A.M.)
Moderator: **Philip L. de Bruyn**, M.I.T.
Discussion Leader: **Everett A. Jenne**, U.S.G.S.

Solution–solid exchange reactions of inorganic species. A discussion of kinetic and equilibrium factors affecting the sorptive accumulation of inorganic species at solid–water interfaces. Consideration of the surface characteristics of selected solids and how these affect the sorption process.

Session 1.2 (P.M.)
Moderator: **Walter J. Weber, Jr.**, Univ. of Michigan
Discussion Leader: **Douglas W. Fuerstenau**, Univ. of California, Berkeley

Solution–solid exchange reactions of organic species. A discussion of kinetic and equilibrium factors affecting the sorptive accumulation of organic species at solid–water interfaces. Consideration of the surface characteristics of selected solids and how these affect the sorption process.

Tuesday: 2. Coagulation–Flocculation

Session 2.1 (A.M.)
Moderator: **Ronald Packham**, Water Research Assoc.

Discussion Leader: **James J. Morgan**, Calif. Inst. of Technology

Surface reaction in coagulation. A discussion of interfacial forces and mechanisms involved in the coagulation or flocculation of colloidal systems.

Discussion Leader: **Warren J. Kaufman**, Univ. of California, Berkeley

Physical parameters in coagulation. The influence of the hydrodynamics of a system on particle growth kinetics, state of dispersion, and other factors.

Session 2.2 (P.M.)
Moderator: **Jesse M. Cohen**, F.W.P.C.A.

Discussion Leader: **Egon Matijevic**, Clarkson College of Technology

Chemical parameters in coagulation. A discussion of how the coagulation process is affected by solution composition, primary coagulants, coagulant aids, and the like.

Wednesday: 3. Filtration

Session 3.1 (A.M.)
Moderator: **Sheldon K. Friedlander,** Calif. Inst. of Technology
Discussion Leader: **Kenneth J. Ives,** Univ. College, London

Surface reactions in filtration. A discussion of interfacial forces and mechanisms involved in the filtration of particulate and colloidal fractions from water.

Discussion Leader: **Charles O'Melia,** Univ. of North Carolina

Relationships between surface reactions and physical aspects of filtration. An attempt to define the relative significance of surface forces and gross physical effects in sand filters.

Session 3.2 (P.M.)
Moderator: **J. A. Borchardt,** Univ. of Michigan
Discussion Leader: **John L. Cleasby,** Iowa State

Practical considerations in filtration applications. A consideration of the functions of filtration processes in water and waste water treatment, with particular emphasis on the inter-relationship between filtration and coagulation operations.

Thursday: 4. Membrane Processes
Session 4.1 (A.M.)
Moderator: **A. S. Michaels,** Amicon Corp.
Discussion Leader: **Harry P. Gregor,** Brooklyn Polytech.

Surface characteristics of membranes. A discussion of the role of surface forces in membrane process—types of membranes and the relative significance of surface forces as a function of type.

Discussion Leader: **Robert N. Rickles,** Celanese Corp.

Mechanisms of mass transfer. A consideration of mechanisms by which inorganic and organic substances undergo transport across membranes, and how surface properties of membranes affect the transport process.

Session 4.2 (P.M.)
Moderator: **K. S. Spiegler,** Univ. of California
Discussion Leader: **Ulrich Merten,** General Dynamics

Membrane applications. A discussion of the application of membrane processes to water and waste water treatment, including detailed consideration of limiting factors and conditions.

Friday: 5. Presentations Originating from the Conference

Moderator: **Gordon Robeck,** U.S.P.H.S.

The Friday morning session will be kept open for presentation of discussions originating during the conference. Any persons wishing to make a presentation on Friday morning will so inform the conference chairman by Thursday morning to allow time for scheduling for Friday morning.

Persons interested in attending the conference should contact Dr. W. George Parks, director, Gordon Research Conferences, University of Rhode Island, Kingston, R.I. 02881, to obtain additional information and application forms as soon as possible. Attendance at the conference is limited to approximately 100.

PROFESSIONAL CONSULTING SERVICES

MEETING GUIDE

February 18–21, 1968
American Institute of Chemical Engineers

63rd National Meeting
   Chase Park Plaza Hotel, St. Louis, Mo.
The meeting comprises symposiums on petrochemicals, pharmaceuticals, materials, computers, chemicals for agriculture, and other topics of interest to environmental specialists. Special papers will be delivered on fuel cells, separation techniques, and waste transport in river systems.

February 19–22, 1968
Technical Association of the Pulp and Paper Industry

53rd Annual Meeting—7th Pulp and Paper Industry Exhibit
   Hilton Hotel, New York, N.Y.
Among the 20 sessions scheduled for the meeting is a discussion on odor abatement. The 7th Pulp and Paper Industry exhibit will be held during the first three days of the meeting and will feature air and water treatment equipment, and instruments for measuring and controlling air and water pollutants.

March 3–8, 1968
Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy

19th Annual Conference
   Cleveland Convention Center, Cleveland, Ohio
The theme of the 1968 conference is analytical chemistry and spectroscopy for the future. The conference will feature symposiums on specific ion electrodes and the role of government and industry in pollution control. Exhibits from more than 200 companies will highlight the latest in analytical instrumentation.

March 4–6, 1968
Society of Toxicology

7th Annual Meeting
   Shoreham Hotel, Washington, D.C.
The meeting plan is for a series of sessions that treats such subjects as insecticides and cyclamates; effects in dogs on inhaling vapors of chlorinated hydrocarbons; various effects on laboratory animals after exposure to a variety of chemicals; chemical carcinogens; and metabolism of pesticides. Also planned are reports on pesticide and detergent toxicity studies; liver function after exposure to hepatotoxic chemicals; turpentine-induced changes in the lung; and reserpine-induced gastric lesions in rats. There will be a symposium on toxicological studies in animals of economic importance.

March 17–21, 1968
Central States Water Pollution Control Association
Second Annual
Water Pollution Control
Management Institute

   Allerton House, University of Illinois, Robert Allerton Park, Ill.
Designed to assist managers of water pollution control facilities in improving their management skills, the institute will provide instructions and discussions by leading educators in the field of business management and by well-known administrators in the field of water pollution control. Admission to the institute is by advance registration only. Contact Mr. Leonard A. Montie, secretary-treasurer, Central States Water Pollution Control Association, 1808 Van Hise Ave., Madison, Wis. 53705.

March 27–28, 1968
IIT Research Institute–Bureau of Mines

Symposium on Mineral Waste Utilization
   IIT Research Institute, Chicago, Ill.
The symposium reflects growing national concern about difficulties associated with mineral waste disposal. The meeting also reflects growing realization of benefits that can be gained from utilization of such wastes. Presentations, highlighting current efforts to develop methods for recycling and using mineral wastes, will be directed to aluminum ores, phosphate slimes, coal wastes, iron ore wastes, copper wastes, furnace slags, and others. Included will be the economic, ecological, and systems aspects of the problems associated with such disposal.

March 28–29, 1968
Clemson University Council on Hydrology

Hydrology in Water Resources Management
   Clemson University, Clemson, S.C.
The conference focuses on hydrologic problems as they relate to water resources development in the southeast, and will include informative papers on related topics. Contact Prof. R. A. Banister, coordinator, Office of Industrial and Municipal Relations, Clemson University, Clemson, S.C. 29631.

March 31–April 3, 1968
Desert Research Institute of University of Nevada

Symposium on Erosion as Related to Air and Water Pollution
   Stardust Hotel, Las Vegas, Nev.
The theme of the symposium is the mechanics of erosion as it is related to air and water pollution. The symposium is sponsored by Kennecott Copper Corp., Golden Bean Oil Co., American Meteorological Society, and Desert Research Institute. Topics include physics of soil erosion by air movement, water erosion and erosion cycles, meteorological aspects of soil erosion, medical aspects of airborne particulates, and others. A planned field trip to Death Valley will afford an opportunity to examine various areas affected by both wind and water erosion.

March 31–April 4, 1968
American Institute of Chemical Engineers

1st Materials Engineering and Sciences Exposition and Conference
   Sheraton Hotel, Philadelphia, Pa.
Aware of the fact that one third or more of chemical engineering graduates are actively engaged in the field of materials, AIChE has planned 13 symposiums on various materials oriented subject areas.

March 31–April 5, 1968
American Chemical Society

155th National Meeting
   San Francisco, Calif.
The ACS National Meeting will feature a full week's program on environmental subjects. A first symposium on Developments in Petroleum Environmental Chemistry will be co-sponsored by the Divisions of Petroleum Chemistry and Water, Air, and Waste Chemistry. This symposium will include the chemical characterization and control of aqueous and gaseous wastes from the production, refining, distribution, and use of petroleum products. A second symposium on Instrumental and Automated Methods of Chemical Analysis for Water Pollution Control will be co-sponsored by the Divisions of Analytical Chemistry and Water, Air, and Waste Chemistry. A third symposium on Radionuclides in the Environment will be sponsored by the Division of Nuclear Chemistry and Technology and will include papers on aerosols and atmospheric transport. In addition, general papers on such things as air, water, saline water conversion, photochemistry in air pollution, and mass spectrometry applied to the study of atmospheric reactions will be presented.

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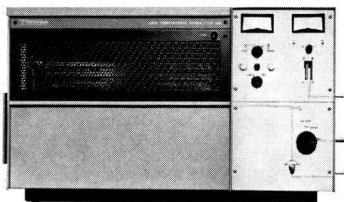
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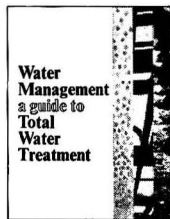
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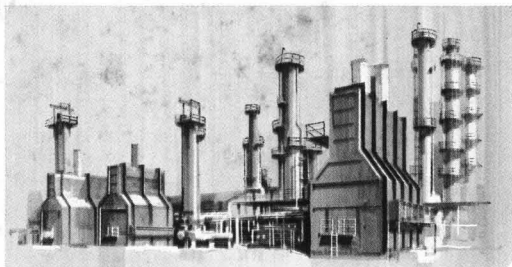
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