



# ENVIRONMENTAL Science & Technology

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*Water,*

*Air, &*

*Waste*

*Chemistry*

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JANUARY 1967

Environmental studies for  
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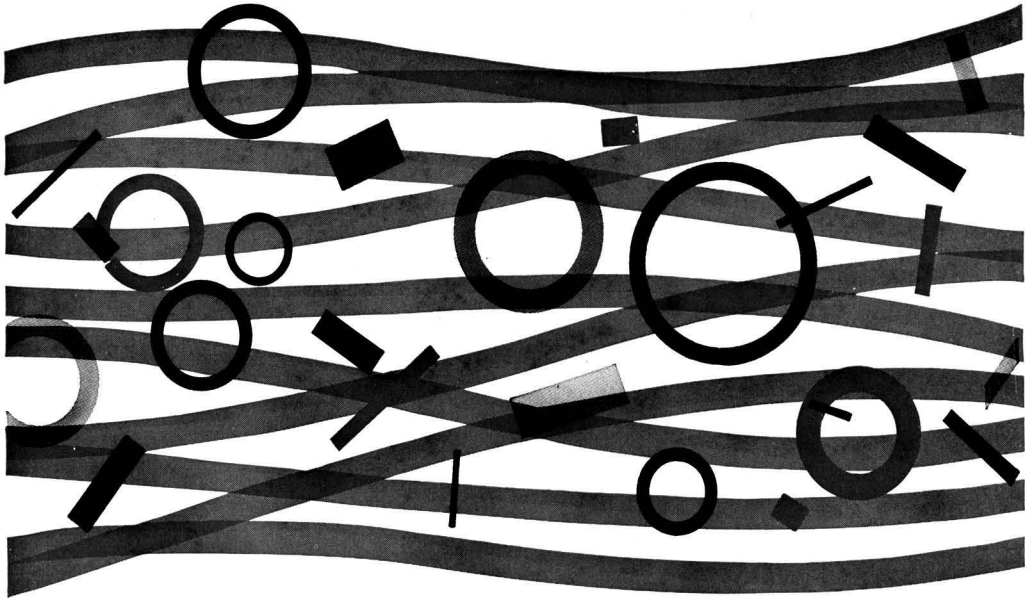
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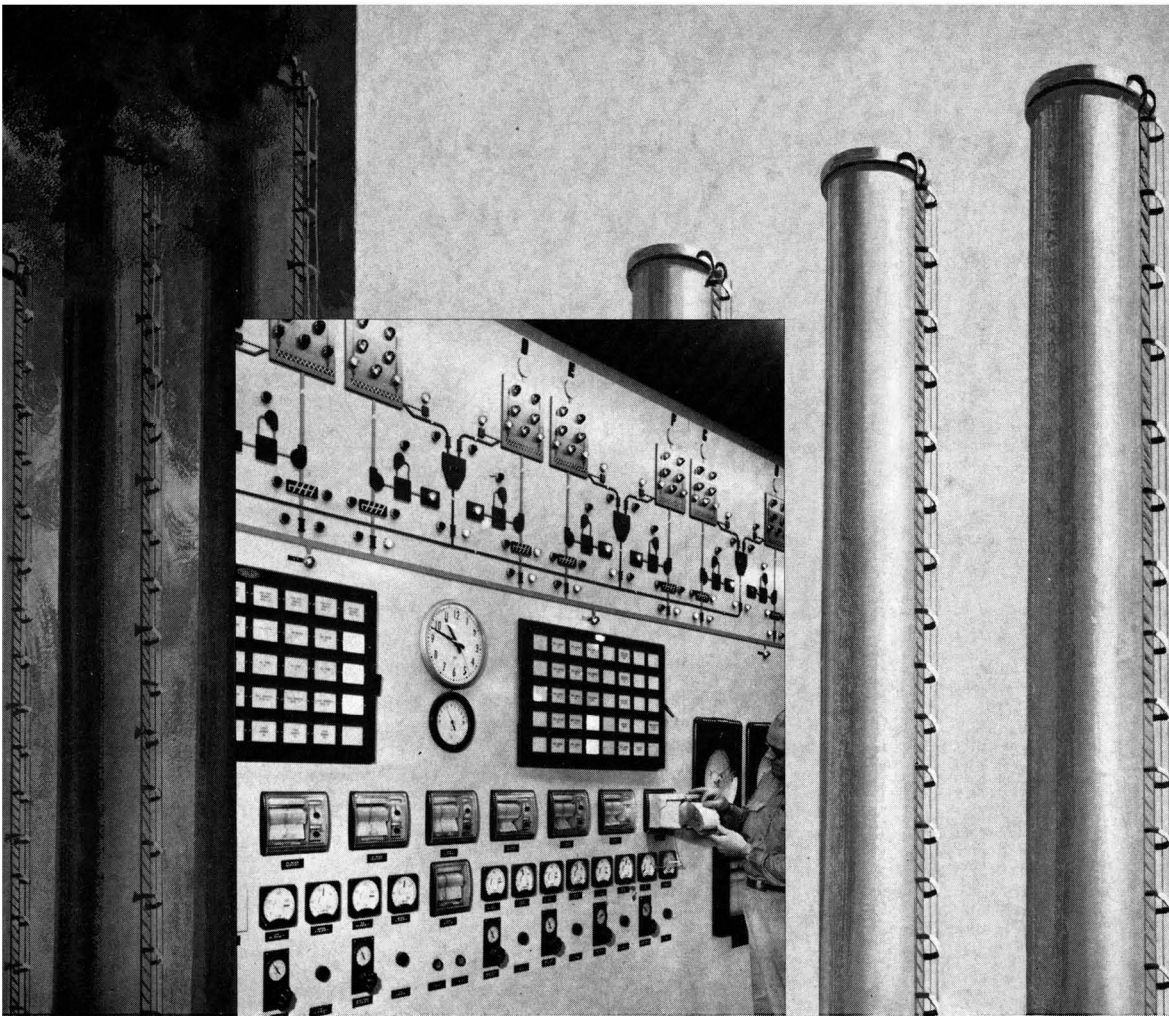
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January 1967

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J. T. Cookson, Jr., and W. J. North 46

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# EDITORIAL

## Chemistry and the quality of man's environment

Chemistry has a major role to play in understanding the water, air, and land environments and in preventing their degradation. The Division of Water, Air, and Waste Chemistry of the ACS has made significant efforts through its research programs and symposiums to advance sound chemical approaches to natural water quality, air pollution phenomena and their control, and the technology of domestic and industrial water and waste treatment.

In recent years, successful efforts in the development of joint research symposiums between the Division of Water, Air, and Waste Chemistry and other divisions of the ACS (Colloid and Surface Chemistry, Agricultural and Food Chemistry, Chemical Education) and in the organization of multidisciplinary programs within the division itself ("Equilibrium concepts in natural water systems," "Capacity of streams to assimilate wastes") have underscored the interdependence of research knowledge from chemistry and from other disciplines concerned directly or indirectly with the quality of the environment.

As a journal of chemical research, ENVIRONMENTAL SCIENCE AND TECHNOLOGY will strive to foster those exchanges between the various branches of chemistry and between chemistry and other sciences which have seen such encouraging beginnings in the work of the Division of Water, Air, and Waste Chemistry of the ACS.

As scientists we are coming more and more to recognize that the exercise of ecological foresight in the face of technological change cannot be based upon one field of science alone. The biosphere and the land, air, and water environments are all coupled in one way or another. The role and significance of chemistry in the study and control of the environment are often linked to other physical, biological, or social sciences.

In the publication of research papers, ENVIRONMENTAL SCIENCE AND TECHNOLOGY will place particular stress upon advances in chemistry and chemical technology in relation to the understanding of the nature of the natural environment and control of environmental pollution. It will focus as well on the relationship of chemistry to other branches of science and technology which contribute significantly to the understanding and control of man's environment.

The journal will publish critically reviewed research papers which represent significant scientific and technical contributions to our understanding in all relevant areas within the broad field of environmental science and technology. The research pages are thus devoted to all aspects of environmental chemistry, and especially water, air, and waste chemistry, and to significant chemically related research papers from such other fields as biology, ecology, economics, meteorology, climatology, hydrology, geochemistry, limnology, toxicology, biological engineering, medical sciences, marine science, and soil science, as these may contribute directly to increased understanding and control of man's environment.

Scientific understanding of the environment and the development of chemical technologies for environmental control are not ends in themselves. The goal is the benefit of man. Society must decide, in the light of the best information that science can provide, what kind of environment it wants. Significant questions of economics and policy are involved in these decisions. For these reasons, in addition to research papers, reviews, and communications, ENVIRONMENTAL SCIENCE AND TECHNOLOGY will work to keep its readers abreast of important technical, economic, and political developments, and it will contain the viewpoints of technically qualified individuals from different fields on significant environmental problems and policies.

James J. Morgan

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### **Joint Great Lakes Effort**

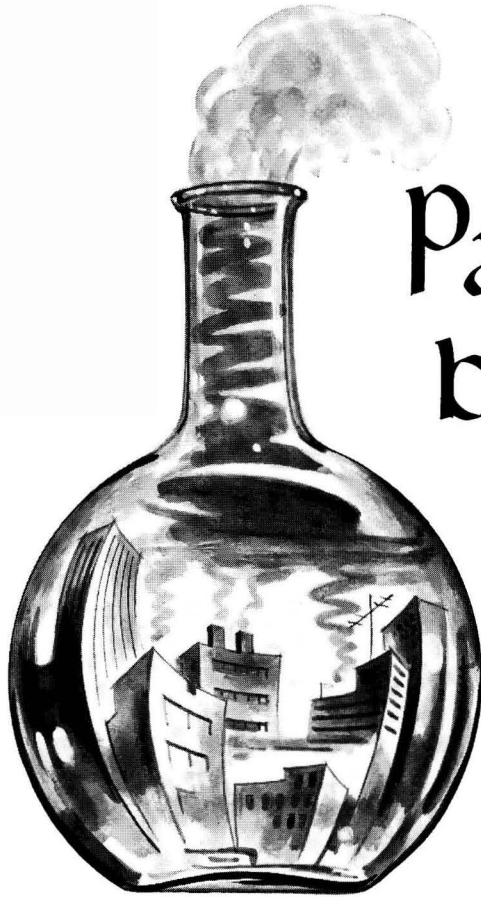
U.S. and Canada join forces to study the Great Lakes. The largest system of fresh water in the world, the Great Lakes will be the subject of a joint 18-month scientific investigation starting in April 1970. The project is known as the International Field Year on the Great Lakes (IFYGL) and is a cooperative program of the U.S. and Canadian National Committees of the International Hydrological Decade (IHD). IHD (1965-74) is a cooperative program in which about 90 countries are working to add to the world's basic knowledge about water, with emphasis on national, continental, and global water systems. Although IFYGL plans to study all the Great Lakes, its attention will probably be focused on Lake Ontario because it is accessible to hydrologists for year-round study and because the shoreline is already dotted with monitoring stations. IFYGL's steering committee, however, is considering the possibility of studying Lake Superior in detail and the final decision between the two lakes has not yet been made. The IFYGL program will be largely restricted to basic hydrological studies, but the planners expect to add substantially to knowledge about the entire range of fundamental processes affecting the lakes. One of the goals of the study will be to provide insight on how to manage the destructive effluents, how to anticipate and control water levels within the Great Lakes system, and how to interpret and use data on the energy balance in the Great Lakes area in understanding its relationship to the weather along the shores and the problems related to the formation and dissipation of ice on the lakes.

### **Limestone for SO<sub>2</sub> Capture**

Limestone is effective in removing sulfur dioxide from burning coal or oil. According to a preliminary report from Battelle Memorial Institute (under contract to HEW), thermochemical calculations to determine what reactions occur in the various furnace atmospheres and temperatures, kinetic studies of the rate-controlling features of the reactions, and analysis of the potential engineering problems provided some answers to the 30-year-old question: Can limestone be added to a furnace to capture sulfur dioxide? The answer is yes, says W. T. Reid who headed the Battelle-Columbus study team. For coal-fueled systems the limestone probably should be added where the flue gases enter the superheater and reheater sections, with the limestone being ground as fine as possible. Small amounts of iron oxide, serving as a catalyst and increasing the overall rate of sulfur dioxide capture, increase the effectiveness of the limestone. For oil-fired furnaces, powdered limestone can be injected directly into the flame region. The Battelle study is based largely on theoretical calculations, and suggests that the typical coal-fired boiler furnace of a 500-megawatt power station, burning 5000 tons of coal per day with an average 3% sulfur content, would produce nearly 300 tons of sulfur dioxide per day, requiring a minimum of 465 tons of powdered limestone for complete capture.

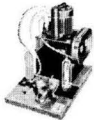
### **Ground Water Shortage**

Ground water levels and streamflow are below normal for this time of year throughout much of the Northeast. Hydrologists of the Geological Survey (Dept. of the Interior) say that though there are few, if any, critical water supply problems now, it is possible that some parts of the Northeast may enter the 1967 growing season with a deficiency of ground water storage. Ground water, which the survey has described as the U. S.'s main reserve of fresh water, supplies between one fifth and one sixth of the nation's total water use.



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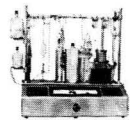
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### **Acid Mine Pollution**

January 1 was the deadline for all Pennsylvania coal operators to obtain new drainage permits from the State Sanitary Water Board or to cease mining operations. New permits were granted only if the board was satisfied that the operator had eliminated or was taking "expeditious action" to eliminate acid mine pollution at the earliest possible date. Meanwhile the board said that it is recommending to the state and federal governments that funds be made available for the treatment of water discharged from abandoned mines to protect active mining operations.

### **Phenol Removal from Water**

Phenols are removed from refinery waste water in a new process developed by Humble Oil. The process, already in use at Humble's Baton Rouge, La., refinery is based on the differential solubility of phenol in oil and water. Cat cracker distillate water containing phenolic material leaves the cat cracker and is mixed with a light catalytic cycle oil. The oil and water streams mix in line, the oil picking up the phenol from the distillate water because of the greater solubility of phenol in oil than in water. The mixed stream goes to a separation drum where the normal gravitational separation of oil and water is enhanced by the presence of an intense electrostatic field. After separation the cleaned water is passed into a refinery drainage line and the phenol-loaded catalytic oil is cycled to a phenol recovery system. Humble, which expects the process to find wide use in the chemical, petroleum, and allied industries, says that Esso Research and Engineering Co. will license the new process through Howe-Baker Engineers, Inc., Tyler, Tex. Howe-Baker will design, engineer, and manufacture necessary equipment.

### **Water Pollution by Erosion**

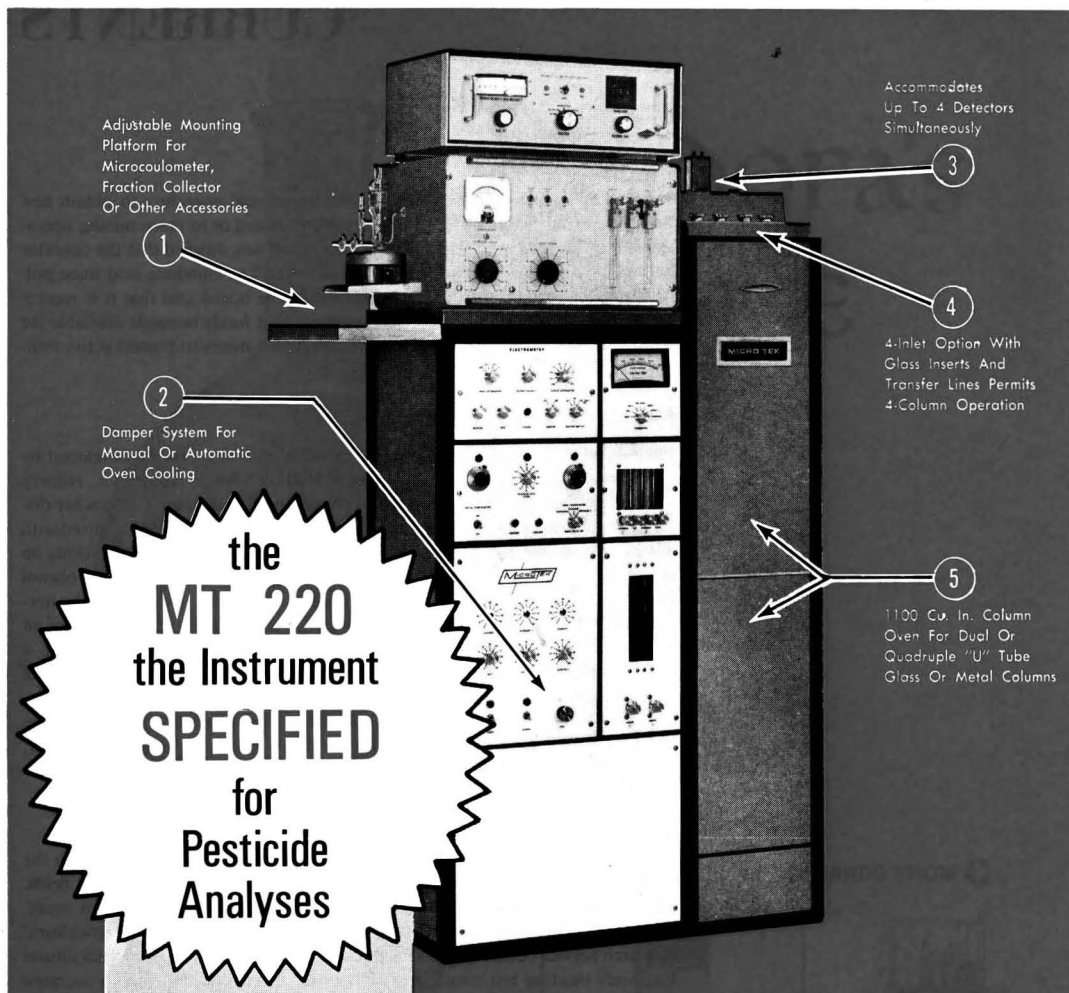
Erosion may be the main cause of water pollution. Uncontrolled erosion in the U.S. produces nearly 4 billion tons of sediment annually from farm fields, gullies, stream banks, highways, and construction sites around urban areas, Dwight W. Smith, assistant director of water management for the Agricultural Research Service (USDA) told attendees of the American Society of Agricultural Engineers meeting last month in Chicago, Ill. Chemicals that are an accepted and necessary part of the production processes on modern farms are adsorbed on the clay or organic fractions of the soil and, during the erosion processes, ride along to streams and lakes, he said. Topographic modification and mulching with crop residues are valuable tools for erosion control on modern grain farms. Much study is under way in such problem areas, with nearly \$4 million a year being spent on research on erosion, sedimentation, and control practices.

### **Solid Waste Disposal**

Abandoned strip mines in Maryland will be used for disposal of solid wastes, including all types of solid refuse except sewage. The three-year demonstration project, supported by Maryland and the U.S. Public Health Service, will help alleviate the state's mounting trash problems and may serve as a guide to the solution of similar problems elsewhere. Two side benefits may be reclamation of scarred landscape and elimination of acid mine drainage which is polluting surface water. Allegany County (Md.) has already leased a small strip mine for the test, which will include studies on costs, procedures, precautions needed to prevent adding to ground or surface water pollution, and the effect that such fill has on acid mine drainage. Some experiments are planned to study the feasibility of disposing of a combination of solid waste and sewage sludge.



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### **ESSA Advisors**

NAS-NAE committee has been set up to advise ESSA. National Academy of Sciences and National Academy of Engineering have established a joint committee to provide continuing advisory services in science and engineering to Environmental Science Services Administration. The committee will operate within the National Research Council's division of earth sciences and will be under the chairmanship of Dr. Verner Suomi, professor of meteorology at the University of Wisconsin. The committee members, covering a range of disciplines that includes seismology, meteorology, oceanography, hydrology, and geodesy, will direct itself to such ESSA problems as to what environmental services are needed, how ESSA can best provide these services, and what scientific areas require research to help ESSA provide better services. For more on ESSA see article on page 14.

### **Great Lakes Air Pollution**

The International Joint Commission (U.S. and Canada) has appointed two advisory boards to assist in the technical investigation of the problem of air pollution in the vicinity of Port-Huron-Sarnia and Detroit-Windsor. The advisory boards are charged with examining the air in these areas to determine if the quantities of air contaminants present are detrimental to the public health, safety, or general welfare of citizens or property. On determining that such air pollution exists, the advisory boards are directed to determine the sources of the pollution, to recommend preventive or remedial measures most practical from economic, sanitary, and technological points of view, and to estimate the total cost of implementing the recommended measures. IJC has also been requested to note air pollution problems in boundary areas elsewhere along the common border and to draw such problems to the attention of both the U.S. and Canadian governments.

### **National Health Center**

The first of this year the National Center for Urban and Industrial Health started operations. Located in Cincinnati, Ohio, the new center is part of the Public Health Service's new Bureau of Disease Prevention and Environmental Control. The center will focus attention on the prevention and control of environmental hazards and health problems associated with urban living, transportation, and industry. Jerome H. Svore, who previously held the rank of sanitary engineer director in PHS, has been named director of the new center.

### **Fly Ash-SO<sub>2</sub> Scrubber**

Simultaneous removal of fly ash (98%) and sulfur dioxide (91%) has been achieved at Wisconsin Electric Power Co.'s Oak Creek plant. The wet scrubber system, which uses sodium carbonate solution as the scrubbing liquid, was described by W. A. Pollock and Garry Frieling of Wisconsin Electric Power Co. and James Tomany of WOP Air Correction Division (Greenwich, Conn.) at the annual meeting late last year of the American Society of Mechanical Engineers. Investment costs of about \$10 per kilowatt and operating costs of \$1.17 per ton of coal are required for a plant having a generating capacity of 25 megawatts and producing 100,000 cubic feet per minute of flue gases at 300° F. Operating pressure drops in this system were about 4.5 inches w.g.

# ESSA, Environmental Innovator and Catalyst

*Born either 10 decades too late or half a decade too soon, ESSA nonetheless is on the scene—a precocious 18-month-old, full of promise, but getting into everything*

“Environment” is a distinctly easy idea to promote a cause with these days. It spawns new university departments, new branches state health agencies, new journals and newsletters, and new federal agencies. The reason is simple enough. Environmental quality—whether it be medical, urban, recreational, or the common garden variety—is not only a politically chic but wholly legitimate issue in a society that is sensitive to its problems and can afford to tackle them.

Better quality of the surroundings is definitely in the cards for the final third of this century. The unknown quantity is the way our various institutional structures are destined to pull it off with, and independent of, the Federal Government.

This will be a continuing narrative that ES & T will relate as the federal, state, community, educational, and industrial patterns shift and flow.

For now, anyway, one intriguing matter dominating environmental gossip is the actions, interactions, and intentions of the Commerce Department's Environmental Science Services Administration, otherwise known as ESSA. It seems that the mere creation of ESSA more than 18 months ago set the environmental policy pot aboil in several other agencies, such as the National Science Foundation, Geologic Survey, Bureau of Reclamation, and Navy Oceanographic Office. It has forced the Government to examine whether its established institutions are organized properly for a systematic assault on environmental problems.

## ESSA's charge

What, precisely, is ESSA? Any federally attuned environmentalist knows by now that ESSA is an amalgamation of

the Weather Bureau, Coast and Geodetic Survey, and Central Radio Propagation Laboratory. According to President Johnson's directive establishing the triune, ESSA's goal is to be “a single national focus to describe, understand, and predict the state of the oceans, the state of the upper and lower atmospheres, and the size and shape of the earth.” In addition, ESSA has taken it upon itself to perform a better job than had been done in warning the public of such natural hazards as hurricanes, tornadoes, seismic sea waves, floods, and earthquakes.

Impressive economies were to be achieved through merger of Weather Bureau and CRPL instrumentation and aircraft and C&GS seacraft, since ocean-atmosphere and atmosphere-ionosphere interface dynamics generate much of the earth's weather dynamics.

ESSA, indeed, looked good philosophically, pragmatically—and on paper. The only troubles were that word *environment* and those four institutes (earth, atmospheric, oceanographic sciences, and telecommunications sciences and aeronomy) ESSA quickly formed, particularly the one on the earth sciences.

## Cross purposes

Environment is a mighty big word for a single federal agency to use because several agencies are scientifically environmental in one way or another. And when ESSA created the institutes of earth sciences, atmospheric sciences, oceanography, and telecommunications sciences and aeronomy everyone started wondering whether ESSA was some sort of modern day political re-enactment of Alexander the Great's drive toward empire.

According to most evaluations,

ESSA's bumptiousness was more imaginary than real. While it has made plays for all civilian mapping functions and for major responsibilities in earthquake studies and prediction (losing both bids), ESSA was conceived in innocent enthusiasm as a grand idea with thoughts of encroachment limited only to some of its more exuberant people.

This isn't to say ESSA wouldn't appreciate a little gift of, say, the Geological Survey and the Goddard Space Flight Center to round out its capabilities. But such bestowals simply are not in the works while President Johnson has the poverty program, Vietnam, and re-election weighing on his mind. Enough people already have schemes for Interior Department reorganizations and all such plans involve the retention of the scientifically rich Geological Survey.

Some of the Government's environmental observers see ESSA, in fact, absorbing the National Oceanographic Data Center within a year or two. Currently belonging to no one, administered by the Navy, and run by a less than ideally coordinated inter-agency committee, NODC's staff labors under an understandable sense of homelessness. Indeed, the recent appointment of former NODC chief, Dr. Woodrow C. Jacobs, to head ESSA's Environmental Data Service makes such a shift all the more likely. And the NODC staff appear to welcome such an embrace, since ESSA's fine meteorological data systems would lock neatly into analogous data that NODC gathers, but does not integrate, from the oceans. The crucial decision apparently rests with the Council on Marine Science, Resources, and Development established by law last year to chart the nation's oceanographic future.



**Robert M. White**

*Nation faces whole new problems*

At any rate, ESSA is doing no overt campaigning for larger dimensions. It's got too many organizational and scientific problems to concern itself with. Taking NASA or the Geological Survey head on could cripple both its operations and reputation.

#### **ESSA's scope**

A partial inventory of ESSA's current interests goes something like this:

- Weather modification, highlighted by hurricane control through silver iodide seeding (Project Stormfury), various rainmaking experiments around the country, and a growing program of basic research in all facets of weather and climate control. The Weather Bureau, never very aggressive in promot-

ing positive research in weather control is now faced with recapturing lost opportunity.

- Environmental pollution. Just beginning, as ESSA works to seek a role in this bandwagon endeavor. Since the Weather Bureau predicts stream flow, ESSA sees itself predicting the concentration of pollutants in streams and lakes. And since the Coast and Geodetic Survey predicts tides and does research on sea water properties, ESSA envisions a growing role for itself in ocean and estuary pollution studies.

- Earthquake reporting and prediction. The Coast and Geodetic Survey records earthquakes through a series of seismographic stations and warns of seismic sea waves. ESSA wants to do more. It seeks to determine the actual

cause of earthquakes. So does the Geological Survey. So far each has gone its own way, but any future showdown should register on a few bureaucratic Richter scales.

- National Natural Disaster Warning System. No one can fault this ESSA extension of what essentially is patterned after the highly successful hurricane warning network. The communications net of telegraph centers, and local radio stations, is actually in place for quick issuance of flood, hurricane, tornado, tidal wave, and other warnings.

- Environmental Data Center. This is what many of ESSA's critics say the agency ought to concentrate on. NASA, for example, has little idea of the quality of atmospheric data collected and stored by scores of satellites sent aloft during the past nine years. Neither has anyone else. ESSA would like to tackle the chore of analyzing the data. To a lesser degree, the same holds true for oceanographic data despite the commendable work of collecting performed by the Navy Oceanographic Data Center.

- Relating environmental data to the economy and the public welfare. For example, an ESSA study showed recently that America's construction industry could save \$500,000 a year through proper use of Weather Bureau information. Other such studies will soon be in progress. One similar report on ESSA's role in developing the resources of the continental shelves was prepared for ESSA by the Battelle Memorial Institute, acting as a consultant. This was much more theoretical than the building study, however, and some wondered why the continental shelves priorities of other agencies weren't brought in.

For fuller perspective, it helps to view ESSA in the larger context of its parent

department, Commerce, which currently is in the throes of a metamorphosis toward greater emphasis on scientific and technological services. Needed, too, is a careful look at what the Interior Department is in business for.

Commerce recently lost the bulk of its transportation functions to the new Department of Transportation. This was a large hunk of priorities for Commerce to let go. With that loss, Commerce has become more of a scientific agency than ever, with some 60% of its personnel concentrated in the Patent Office, National Bureau of Standards, the Census Bureau, and ESSA. Moreover, Commerce administers the State Technical Services Act which is designed to upgrade the technical base of various regions, much as the Agriculture Department helps farmers with its extension services.

Thus, Commerce's philosophy does indeed evolve toward service to an economy that owes its strength and growth to advances in science and technology. Furthermore, the economy hungers for precision and prediction.

But an economy is only as strong as the natural resources it can harness, and natural resources are the Interior Department's domain. Commerce might legitimately promote the flow and marketing of these resources, but Interior finds them, defines them, tells the economic institutions where they are, and often regulates the rate and character of extraction.

Basic environmental studies enter here through various avenues—all, however, relating to the land. In simple terms, the Geological Survey has little need for some of the geophysical data ESSA aspires to provide. But it does, indeed, need weather reports, tide schedules, depth charts, instrument standardization, economic and population statistics, and certainly an all encompassing warning system for all natural hazards. The Commerce Department supplies it all and no one quarrels with the arrangement.

#### **Mission limited**

Many in the government, including top ESSA officials, say ESSA is out only to supply environmental data needs—that is, to fill gaps in data collection and communication. Under this definition, ESSA, the agency set

up to study man's limitless environment, limits itself because the missions of other "environmental" agencies are set already. The Geological Survey, for example, is an "environmental science service agency" and could well be supplying its own geophysical data to help ESSA better warn of seismic sea waves.

As one highly placed government official pointed out recently, ESSA may have come along 10 decades too late. It could have caught on quickly during the time, 100 years ago, when the nation was wrestling with organizing itself for environmental surveys.

Now missions are pretty well set. Only agencies, not missions, can be transferred. So in this sense, ESSA may not be 10 decades late, but rather half a decade early. Pres. Johnson has submitted 10 reorganization plans to Congress, all with success. Now he has proposed an eleventh.

This eleventh is a brand new complicating factor in the position of ESSA in the government and centers on the President's proposed merger of the Commerce and Labor Departments into a Department of Business and Labor. As ES&T went to press details of the merger were not available. But on philosophy alone, the feeling in Washington is that ESSA wouldn't fit too snugly into such an arrangement. In fact, the President's next reorganization plan could well be the total excision of ESSA from Commerce, creating an entirely separate agency with the autonomy NASA, say, enjoys today. Or, perhaps, ESSA would serve as more than a fanciful nucleus for an entirely new "Department of Environmental Sciences" incorporating what at the moment is anybody's guess.

#### **New problems**

For now, ESSA's fortunes ride on the philosophy of its director, meteorologist Robert M. White whose earliest scientific training was in geology. This is what he said in an interview last month: "I think the nation is beginning to come to grips with whole new problems that weren't as important as in the past: poverty, transportation, man in his environment. They all bear on the question of how man is going to live in harmony with his environment. Thus, many initiatives in the congressional and executive branches of govern-

ment are being taken. So what ESSA is, I think, is an attempt by the Department of Commerce to organize itself for this in the most effective way. The services ESSA renders now were also important at the beginning of the country. These services are part of the infrastructure of the economy. We want to look at problems from the point of view of the ultimate consumer—the Sunday boater, the builder—and we must put this kind of thing on a more systematic basis." It's this economic input supplied by Commerce Department sources, plus the demographic data supplied by the Census Bureau that ESSA finds itself so dependent on in its ride into history.

What, then, are the implications and the relevance of the Environmental Science Services Administration. The answer, in brief, is that ESSA can function both as an innovator and as a catalytic agent between already existing areas of competency.

#### **New approaches**

While the name ESSA has captured neither the imagination nor the comprehension of John Q. Public, it has raised fundamental issues in government and federalism:

- It has forced government decision makers to think clearly through the complexities involved in planning environmental programs.
- It has aroused a staid, stodgy, but extremely capable Geological Survey into an awareness of 20th century social and political issues.
- It has caused considerable new thinking about the extent of environmental interdependence.
- It has, in general, generated among federal scientists a sense of competition, which they can use.

Given the rock-hard traditions of the Geological Survey, and now its readiness to fight any attempt to switch its jurisdictions to other groups, earth science will likely remain where it is, mainly in the Survey, leaving to ESSA the task of describing and predicting every ripple, current, and other electrical and magnetic impulse generated by earth and captured by it from space. Currently, ESSA isn't pushing very hard to reach any more new horizons—and is probably well advised not to. ESSA has a lot to prove and prefers to shun politics, insofar as possible, as it sets out to do its job.



## Improved Precipitator Avoids Particulate Buildup

*High collector velocity capabilities and an electrode system separate from the collector mean reduced precipitator weight and lower capital costs*

Since its introduction in 1908, the Cottrell electrostatic precipitator has dominated the field of large-scale removal of particulate matter from exhaust gases. In brief, the Cottrell precipitator operates by subjecting particles of suspended matter to an intense electric field which transfers charge to the particles through the ionized gas.

Once charged, the particles travel to a depository electrode in accordance with the induced polarity of the particle. The electric field is maintained by imposing a voltage drop of up to 100 kv. across the electrodes. This is an extreme value, and actual values are usually less.

A typical installation has a precipitation efficiency of about 90% (90% of the particles originally present are removed) and requires about  $\frac{1}{8}$  kva. per 1000 cu. ft. gas per min. Efficiencies may be made to approach 100% as closely as economics permit simply by enlarging the installation.

The geometry of most installations is that of the parallel plate unit but other geometries are sometimes desired. Ion velocities in a "clean" gas are of the order of 100 ft./sec., but when particulate matter is introduced, the "drift" velocities are much lower, depending on the mass of the particle, the magnitude of the induced charge, and the strength of the electric field.

Some of the practical difficulties encountered with the Cottrell precipitators involve the necessity to maintain reasonably clean collector electrodes. A particulate deposit is usually insulating and may materially affect the field strength as well as reduce the arcing voltage of the system. Mechanical and fluid cleaning are normally employed.

A new variation of the Cottrell precipitator has been introduced by Gourdine Systems, Inc., of Livingston, N.J. [*Ind. Eng. Chem.* 58 (12), 26 (1966)],

in which some of the difficulties of the conventional Cottrell apparatus are overcome with a simultaneous reduction in capital and operating costs. At least, such is the claim of the inventors. Since the new system evolved from studies of electrogasdynamic power generation, the system has become known as the electrogasdynamic fume precipitator. It depends for its operation not on the migration of charged particles through a static electric field, but on the result of the space-charge field of the charged particles themselves.

In operation the electrogasdynamic precipitator (EGDP) requires four parts. The particulate laden gas is accelerated through a converging nozzle and passes through an ion source at high velocity where the particulate matter is charged to near electrical saturation. The gas then passes through a dielectric section where the space-charge field acquires maximum value. The dielectric section is usually called the generator.

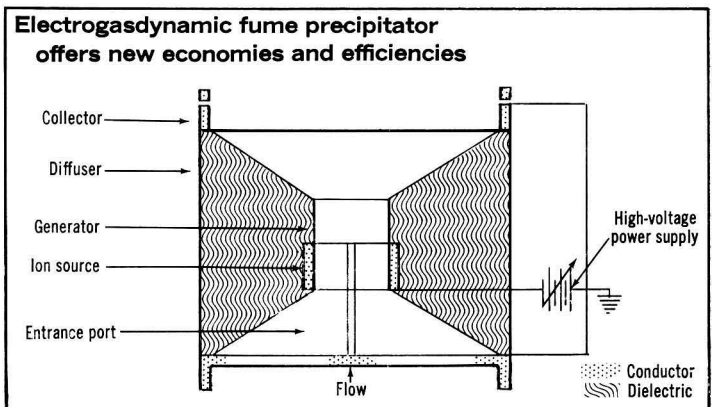
After leaving the generator the stream passes through a diverging nozzle where the net flow velocity is reduced in order to increase the ratio of radial particle velocity to axial particle velocity. The charge field then causes the par-

ticles to repel each other and impinge on the walls of the grounded collector.

Since the collector is not part of the electrode system usually associated with conventional Cottrell apparatus, accumulation of particulate matter does not affect the performance of the apparatus. There is, in fact, neither electrical nor physical connection between the ion source and the collector.

A single-stage EGDP is capable of 90% efficiency, with higher efficiencies possible, depending on the number and size of the stages. High pressures and high temperatures do not affect the precipitator. The higher collector velocities and collector dimensions considerably reduce material weight with consequent reduction in capital costs compared with the usual installations. Another attractive feature is that the small ion source requires only moderate voltages which minimize insulation and power supply problems.

In pilot runs, the inventors have verified performance with flow rates up to 30 cu.ft./min. and dust loadings up to 15 grains/cu. ft. Experiments have been run with fly ash, alumina, oil mists, and carbon smokes with equal control effectiveness.



# POLLUTION LAWS IN THE U.S.

## 20 years of growing federal involvement

*Traditionally handled at the state and local levels, pollution control, is, in effect, now largely directed by the Federal Government. However, Congress and federal administrators seem to be seeking the joint involvement of local, state, and federal governments in controlling pollution through the device of regional compacts*

"Very little pollution has been abated without legislation or litigation or the threat of such action." So said William H. Megonnell, of the U.S. Public Health Service last summer at a conference whose theme was The Demands of Pollution Control Legislation. Traditionally, pollution control was considered best handled at state or local levels in the U.S. But, in recent years it has become increasingly apparent that these jurisdictions could not or would not cope with growing pollution problems. So, the Federal Government, in the decade since the mid-1950's, has assumed a much bigger role in pollution control.

Pollution is not a new problem. What is new is the scope of the problem—and the wide public awareness of it. Increasing industrialization has brought on increasing pollution of land, air, and water. Often interrelated, the various forms of pollution cut across local and state boundaries. The American people, at last aware of the problem, seem ready for strong federal action—and ready to foot the bill, if not directly, then indirectly as hidden charges in the products and services it buys.

President Johnson, on signing the Water Quality Act of 1965, echoed the national awareness of pollution problems when he said "Today, we proclaim our refusal to be strangled by the wastes of civilization. Today, we begin to be masters of our environment."

### Early legislation

One of the earliest attempts at pollution control was a part of the Rivers and Harbors Act of 1899. In its section 13, known as the Refuse Act, it pro-

hibited discharge or deposit into navigable waters of any solid refuse. Its primary purpose, however, was to assist navigation, rather than to control pollution. The Public Health Service Act of 1912 authorized studies of water pollution problems as they affected public health. And the Oil Pollution Act of 1924 sought to control oil discharges from vessels into coastal navigable waters and was designed to prevent damage to aquatic life, harbors, docks, and recreational facilities.

Through the next years many bills were introduced in Congress to define the federal role and responsibility in water pollution control. None became law. In 1936, 1938, and 1940, federal legislation came close to enactment. World War II interrupted these legislative efforts. In 1947, efforts were renewed, culminating in the Federal Water Pollution Control Act of 1948. The first identifiable federal water pollution control law, it served to get the Federal Government involved in national pollution control matters, an involvement that has continued to build in the ensuing years.

When the 1948 act, after several extensions, finally expired in 1956, it was replaced by the permanent Federal Water Pollution Control Act, which remains the basic statutory authority for a comprehensive federal program for the prevention, control, and abatement of water pollution.

The 1956 act declared that states and local governments have the primary responsibility for preventing and controlling water pollution. The federal role, then, was established: to assist the states in fulfilling this responsibility and

to work with the states in solving interstate pollution problems. The 1961 amendments strengthened the act by increasing grants to state and local agencies and by broadening federal abatement authority to include navigable, as well as interstate, waters.

### New federal efforts

By 1965, the public and Congress felt that a larger federal effort was needed. The result was the Water Quality Act of 1965. One of its key provisions was federal water quality standards for interstate waters and portions thereof. For the first time, the Federal Government could act to prevent water pollution, instead of having to wait until pollution created health or welfare problems. Controversy over this key provision delayed passage of the bill by several months. Many industries, as might be expected, feared stricter controls. Other opponents pointed to creeping federal intervention in what had always been considered state matters.

Still, local and state governments were obviously not doing an adequate job of controlling pollution. Sometimes it was the lack of money. Frequently, the authorities simply lacked technical competence. And sometimes it was the powerful opposition of local industry.

The compromise that was finally worked out gave the states the opportunity to set standards, subject to federal (Interior) approval, by June 1967. (By October 1966, all 50 states had notified Interior that they would set their own quality standards and enforce them by June 1967.)

One promising avenue of approach to

the problem of interstate-intrastate relationships is the multistate compact, each of which must be authorized and set up by Congress. Good examples of this approach are the Delaware River Basin Commission (set up in 1961) and the Ohio River Valley Water Sanitation Commission (set up in 1948).

### **Creation of FWPCA**

Another key provision of the Water Quality Act created the Federal Water Pollution Control Administration within the Department of Health, Education, and Welfare. This move sought to give the water pollution program clearer

identification and an administrative status equivalent to that of other major federal water resources activities.

In May 1966, FWPCA was transferred to the Department of Interior. This transfer is indicative of another change evolving in water pollution control efforts. Natural resources have traditionally been in Interior's bailiwick. There, water is a resource, and pollution control is a part of water use and planning. Comprehensive water planning for a river basin or area considers all sources of water, all needs for water, and all effects of usage on water quality.

Social, economic, and political activities are taken into account. The

nation's need for water will continue to expand. In the long run, limited water supplies on a national level will require re-use of water several times, already a regional factor in the operations of many industries. Maintaining water quality is the key to re-use.

The last Congress made its contribution to water pollution legislation, passing the Clean Waters Restoration Act. Following the trend of recent pollution legislation, the act provided for increased funds (for both construction grants and research) and increased federal authority. The act also requires industries involved in pollution abatement proceedings to reveal the quality and quantity of their pollutant discharges at an early stage in proceedings, although the act specifically states that no trade secrets or similar information need be revealed.

## **Chronology of Federal Pollution Control Legislation—Air and Solid Wastes**

### **Air Pollution Control Act (1955)**

First identifiable federal program for air pollution control. Earlier work had been limited, but included Bureau of Mines' studies on pollution from fuel combustion and PHS's studies on such things as the Donora, Pa., episode of 1948. The 1955 act provided for research, technical assistance, and training activities by HEW. The act called attention to the fact that primary responsibility for air pollution control rests with state and local governments, with Federal Government providing leadership and support.

### **Public Law 86-493 (1960)**

Authorized PHS to study the effects that motor vehicle pollution has on health and to report to Congress within two years.

### **Clean Air Act of 1963**

Expanded existing programs. Reiterated policy that primary responsibility for air pollution control belongs to state and local governments, but strengthened the Federal Government's ability to help local authorities to improve control programs. The act ordered HEW to study, compile, and publish criteria on the harmful effects of air pollution agents on health. It authorized grants and provided for a limited federal role in control of specific pollution problems, both interstate and intrastate.

### **Clean Air Amendments and Solid Waste Disposal Act of 1965**

Authorized control of emissions from new motor vehicles. Also, permitted HEW to use existing procedures to abate international pollution originating in the U.S.

In solid waste disposal, the law provided:

- A national research program on solid waste disposal (with part of the program to be handled by HEW, the other by Interior).
- Grants to state and interstate agencies for surveys of solid waste disposal practices and problems. Also, grants to develop disposal plans.

### **Clean Air Act Amendments of 1966**

Authorized federal grants to state and local agencies to operate and maintain programs, equipment, and facilities for effective air pollution control.

### **Investment Tax Credit Suspension (1966)**

Continued, by special exemption, the 7% investment tax credit on pollution control equipment.

### **Federal air pollution control**

The federal air pollution control program started with the Air Pollution Control Act of 1955. Two experiences, one local and specific, the other broader and more general, helped focus national attention on the growing problems of air pollution. The specific instance was the death of 20 people during a brief episode of severe air pollution in 1948 in Donora, a town of 14,000 in western Pennsylvania; many more were made ill. The broader instance was—and still is—the Los Angeles area, where explosive growth of population, automobiles, and industries in the 1940's and 1950's contributed to the area's well known smog problem.

The Los Angeles experience was, perhaps, a blessing in disguise, for it warned the nation of a developing problem that was evolving, although perhaps more slowly, in other cities and towns. Pollution was no longer a problem for a small group of people on the wrong side of the tracks because now everyone was on the wrong side of the tracks. Pollution was no longer a mere nuisance to be settled on a local level. It had become a national problem.

The 1955 act established the basic policy that primary responsibility for air pollution control rests with state and local governments, with the Federal Government providing leadership and support. This is still the policy, although the ways in which the Federal Government can help have changed markedly.

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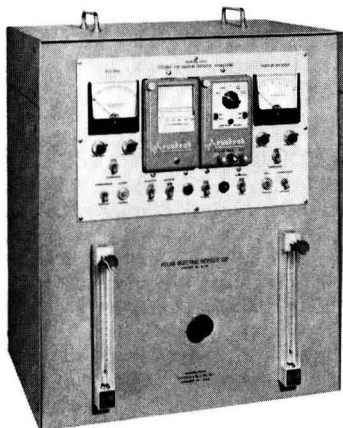
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## Chronology of Federal Pollution Control Legislation—Water

### Federal Water Pollution Control Act of 1948

First identifiable federal program for water pollution control. Limited in scope, it was never fully implemented with adequate appropriations. Government's earlier role had been confined to Rivers and Harbors Act of 1899, Public Health Service Act of 1912, and Oil Pollution Control Act of 1924.

### 1956 Amendments to the Federal Water Pollution Control Act (1948)

Established basic policy that water pollution problems are best solved at the local level. Authorized grants to states and interstate agencies for water pollution control activities; also, grants for waste treatment plant construction. Provided a very limited and complicated system of federal control and encouraged interstate compacts for a joint solution to common water pollution problems.

### Federal Water Pollution Control Act Amendments (1961)

Extended federal pollution abatement authority to all interstate and navigable waters, increased construction grants, and encouraged research activities.

### Water Quality Act of 1965

Provided for the adoption and enforcement of water quality standards for interstate waters and portions thereof. The act set up a separate agency, Federal Water Pollution Control Administration, as part of HEW (FWPCA has since been transferred to Interior). Increased construction grants and authorized R&D grants to develop ways of preventing the discharge of untreated wastes from storm sewers or combined storm-sanitary sewers.

### Clean Waters Restoration Act (1966)

Provided grants for coordinated river basin planning, increased research spending. Also, provided that for a specific pollution conference industrial polluters can be required to reveal quality and quantity of pollutant discharges with the qualification that no trade secrets or similar information need be revealed.

### Investment Tax Credit Suspension (1966)

Continued, by special exemption, the 7% investment tax credit on pollution control equipment.

## New directions

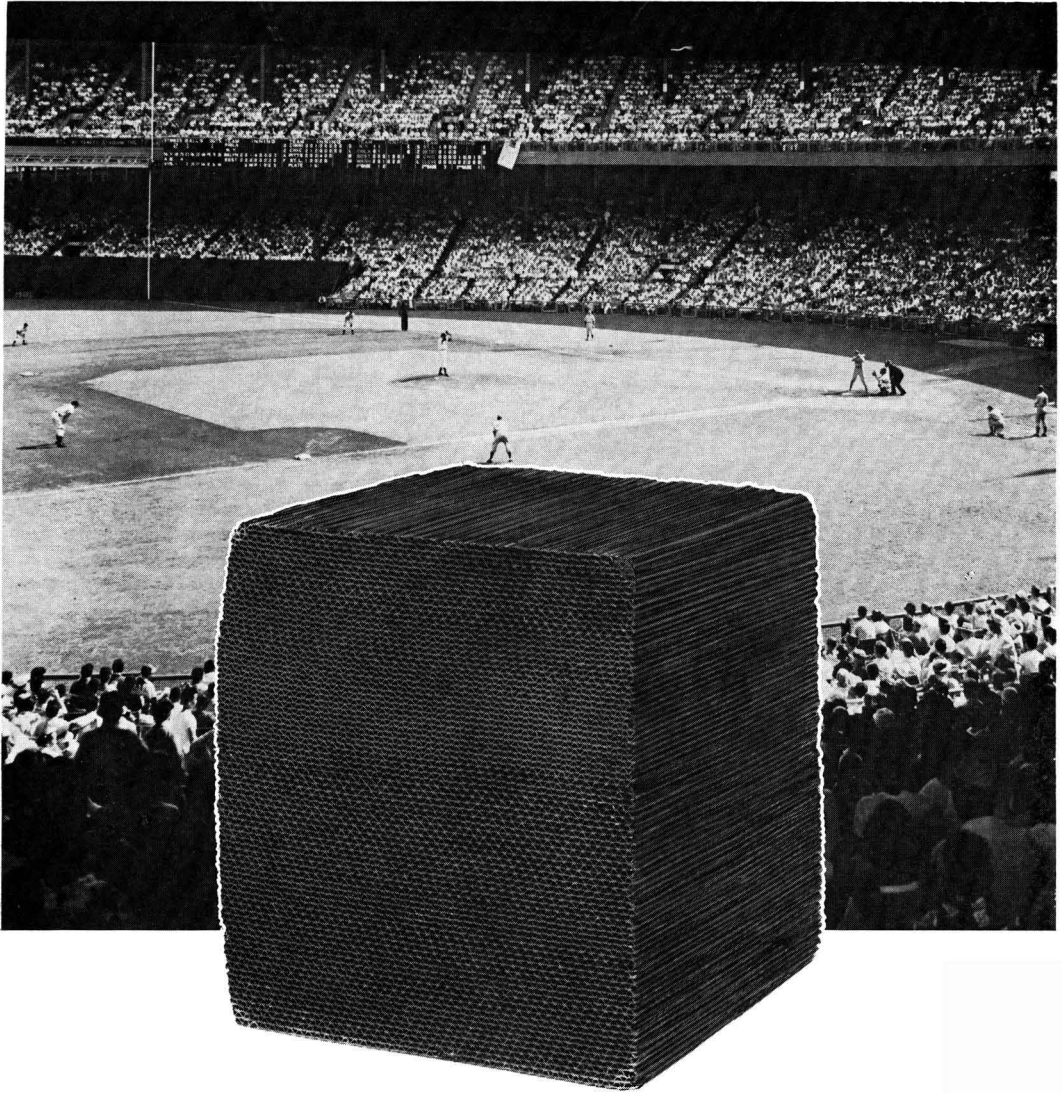
The first eight years of the federal effort added a great deal to scientific understanding of the air pollution problem. But by 1963, most state and local governments were still not equipped to prevent or control community air pollution problems. The Clean Air Act of 1963 sought to remedy these deficiencies by authorizing two major new federal activities:

- Grants to state and local agencies to help them develop, establish, or improve control programs.
- Action to abate specific air pollution problems, both interstate and intrastate. (There are 70 large urban areas in the U.S. which adjoin or overlap state boundary lines; pollution prob-

lems in these areas are essentially beyond the management of individual states and cities.)

## Add automotive exhaust

"In all of the hearings held since the adoption of the Clean Air Act of 1963, automotive exhaust was cited as responsible for some 50% of the national air pollution problem," said a 1964 report of a Congressional subcommittee. Pollution from internal combustion engines was increasing and it was, largely, uncontrolled. Congress recognized this lack of control in 1965 and empowered the Secretary of HEW to set emission standards for new motor vehicles. (In March 1966, the Secretary



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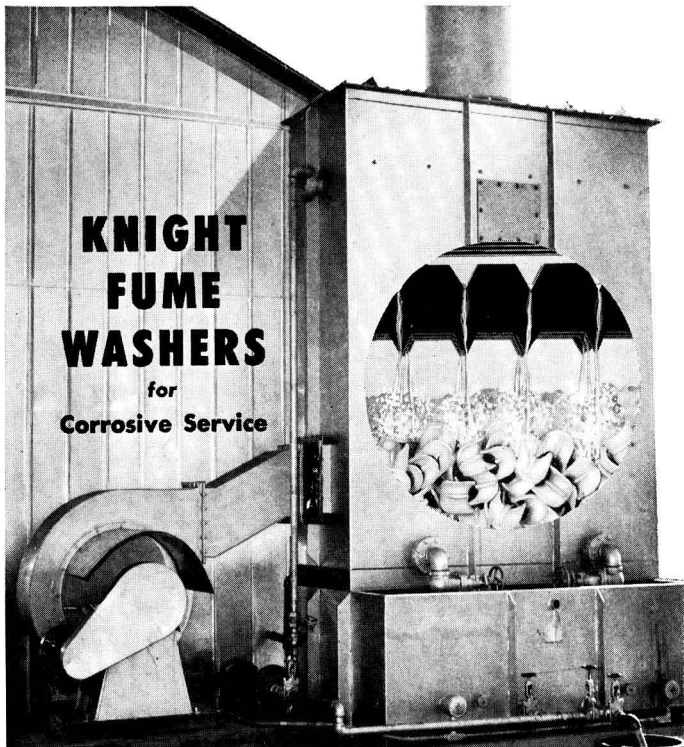
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issued these national standards, to become effective for 1968 models.)

**Plus solid waste controls**

This legislation—the Clean Air Act Amendments and Solid Waste Disposal Act of 1965—recognized still another source of air pollution (and to a lesser degree, water pollution). That same Congressional report of 1964 put it this way: “No more obvious and disgraceful illustration of the need for applied technology can be found than the appalling state in which the Nation’s waste disposal practices exist.”

The 1965 act called for a national research program to find and perfect methods of disposal that would avoid environmental contamination. Hopefully, the research might also turn up methods of recovering salvageable materials lost through primitive disposal practices. The act also provided for grant support for demonstrations and planning of state and local programs.

In 1966 Congress broke no new ground in controlling air and water pollution. Although Congress took no specific action in tightening water pollution control measures, it did authorize the spending of much more money for current pollution control programs. It also approved modest increases in the current air pollution control programs. And it sought to encourage the private sector to embark on a continuing program of pollution control. To this end Congress continued, by special exemption, the 7% investment tax credit on pollution control equipment.

No new major pollution control legislation is likely to come from the 90th Congress. Rather, any efforts in this area will probably be directed to a simple refinement of current pollution control programs. One thing to keep an eye on is a project that Sen. Edmund S. Muskie (D.-Maine) has been refining and testing in public forum, most recently at the three-day HEW air pollution control symposium in Washington, D.C., last month. Simply, Sen. Muskie proposes the creation of a temporary committee on technology and the human environment. Without any legislative authority, the committee will seek to bring scientists and politicians together in a joint effort to study, identify, and then report, with recommendations for action, on potential environmental crises resulting from technological advances.





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# Industry and the Pollution Problem

Both victim and cause of the pervasive pollution problem, industry at the same time has many skills and facilities needed to contribute to the solution of the problem at both the local and national level. Government's role could be to help define the problem and to coordinate and encourage the development of these talents

Industry is vitally interested in discussing the role of private industry in obtaining and developing new technology for pollution abatement because industry has a three-way involvement with the problems of environmental health and pollution.

First, industry is a major victim of the pollution problem. Pollution is an economic liability to industry. In a competitive world, American industry suffers added costs because it must constantly clean the air and water it uses. Investments in plants and facilities lose value as their environment degrades. It becomes harder to attract employees to many once-attractive areas of our country. And, most important of all, damage is done to employee health.

Second, industry is among the causes of the problem. Pollution can be defined as the presence of substances introduced to an environment by man which interfere with his safety, comfort, or health. Outmoded industrial processes, along with the gradual growth of manufacturing methods that seemed harmless on a small scale, have contributed to industry's role as part of the problem. Perhaps even more important, consumers have developed an insatiable demand for many products and services that are simultaneously essential to modern life—and a threat to it.

Third, industry is or can be a major contributor to the solution of the problems, not merely its own environmental problems but those of the entire nation.

Thus . . .

- Industry has the *motivation*. As a major victim of the problem, industry should need no prodding in doing something about it.



**Smog.** Industry is a major victim and cause of pollution

- Industry has the *obligation*. As one of the contributors to the problem, industry should accept its responsibilities, as it is now doing in many localities.

- Industry has needed *skills and facilities*. As suppliers of research data, as designers and builders of instrumentation, as experts in sophisticated new methods of systems analysis, as developers of planned communities, as pioneers in control technology, and as manufacturers of new processes and equipment, American industrial organizations can play an important part, not only in preventing pollution but also in doing the actual job of cleaning our air and purifying our water.

According to a recent estimate, the cost of catching up in pollution abatement and keeping waste management up to date will total \$100 million over the next 10 to 20 years. The chemical industry alone, for example, is spending an estimated 2 to 5% of its total

capital investment for pollution control facilities.

The job of cleaning air and purifying water will be completed most rapidly if attacked on a competitive basis, seeking the most economic solutions and offering a profit incentive to those who learn how to do the job best.

At the same time, it would be folly to suggest that private enterprise alone can solve this massive national problem. There is an urgent need for cooperative action by government—at local, state, and national levels—to establish the permissible limits of pollutants and set the necessary goals and schedules for attaining a healthy—and esthetically satisfying—environment.

To date, the role of the national government in solving the problems of pollution has been to conduct and sponsor research aimed at defining causes and damage, establishing rules and regulations for emission control, and developing new devices and techniques to

monitor and track the sources. Unfortunately, no one is now in a position to establish permissible pollution limitations, or long-range goals and schedules, because the problem is not sufficiently understood.

Congress cannot effectively outlaw cancer, because no one yet knows what causes it. In somewhat the same way, we have this problem with pollution. We know a good deal, but not enough, about what pollutants are in the air, water, and ground. We know a good deal, but not enough, about how they got there. We know very little, and nowhere near enough, about the actual effects of these so-called pollutants on either inanimate materials or living plants and bodies.

For example, I don't believe anyone really knows much about the tolerable limits for, say, ozone in the air before it becomes a health hazard—or the possible consequences of removing all ozone from the air. Perhaps facetiously, it has been suggested that before too many years—if positive action is not taken soon—some of our city dwellers will build up such a natural resistance to smog that they will avoid vacations in the country, where clean air might be too great a shock for their systems.

Certainly, with the possible exception of cancer and heart disease (which themselves may be related to pollution), there are perhaps no problems facing our nation where research is needed as urgently as in the case of environmental health and pollution. For example, relatively little research is still needed to get man on the moon, although no one questions the amount of superb engineering that must yet be done.

But we simply don't have the basic facts needed to launch an all-out assault on pollution. Research—lots of research—is urgently needed. In what areas of science? Who is going to do it? Who is going to pay for it? I will explore these questions briefly.

Basing my comments on research—particularly industrial research—with which I am familiar, I should like to list some of the areas where I think there are good potential opportunities for finding new knowledge that should be helpful.

*Deciding what the problem is.* I have already discussed the immediate importance of this part of the job. It is fortunate that throughout the world of

science—in industrial research and elsewhere—life scientists and physical scientists are learning that they can work much more closely together than they have in the past. The continuing interaction of biology, medicine, and other life sciences with chemistry, physics, mathematics, and other physical sciences should help us to define better the true problems of environmental pollution before we spend too much time and energy on the wrong solutions.

For example, I think the time is ripe for some closed-loop experiments on a large scale. Some of my associates have suggested studies in which constant monitoring of pollutants and suspected pollutants is done over a large populated area. Information from such monitoring would be fed into a large computerized information system. Simultaneously, the computer would be given all possible information about the times and reasons for hospital admissions, reports from medical specialists about the number and severity of cases involving a specific list of diseases and disorders, statistics on absenteeism in school and industry, industrial productivity figures, death and accident rates. We all know the difficulties of establishing cause-and-effect relationships, but certainly if patterns and correlations could be established from such studies, we would have information vital for determining the direction of future research.

*New monitoring and measuring techniques.* Although great progress has been made in building machines that will sniff the air and taste the water, there is still much to be done. For example, we don't know enough about the extremely tiny particles that contaminate the air around us. I refer to particles in the general range of a few millionths of a centimeter in diameter—or less. The surprising fact is that although the particles in air larger than a tenth of a micron constitute some 90% of the total *weight* of all the particles, those smaller than a tenth of a micron constitute some 95% of the total *number* of all particles. More important, the total *surface* area of these small particles at least equals the surface area of the larger particles and in metropolitan areas is many times the surface area. It is on the surface of such particulate matter that waste gases are absorbed—and the fact is that we know little or

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*This article is based on testimony Dr. Bueche gave last year before the Subcommittee on Science, Research, and Development of the U.S. House of Representatives*

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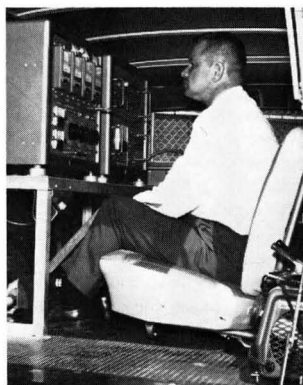
nothing about how, what kind, or how much gas is absorbed by these tiny particles. Remember, too, that the smaller the particles the more likely they are to get into our lungs—and then discharge their contaminants into our bloodstreams.

On the basis of their recent work, some of my associates suspect that these mysterious tiny particles may have played an important role in tragic instances of mass air-poisoning such as those in London and Donora, Pa. After these particles have carried gases deep into the body, some of the contaminants may be released onto single cells. This may leave the cells helpless, or even cause their death. In any event, it has been observed that when many of these particles occur in the air, necessary life functions can be affected seriously. Surely, we must learn more about these particles.

Before leaving the subject of new monitoring and measuring techniques, I should emphasize the need for research and development aimed at making sophisticated laboratory devices economically feasible. It is relatively easy for a legislative body to pass a law prohibiting smokestacks that put "measurable amounts" of sulfur dioxide in the air. It is quite another thing to make such a law meaningful. With sophisticated research equipment, the most infinitesimal and perhaps inconsequential amounts become measurable. In the laboratory, the cost of such measurements may be of little consequence, but in practice, on top of the smokestack, it may be economically difficult to make barely adequate measurements on a continual basis. New instrumentation techniques, combining relative simplicity with extreme sensitivity, are now being developed, and a more intensive effort in this area should pay substantial dividends.

*Systems analysis and management.* I have already touched on this area in my suggestion for closed-loop experiments to seek correlations between pollutants and public health. The experience gained by the aerospace and electric utility industries in recent years has produced a new competence in handling multifaceted problems and optimizing systems. It has been our experience that under the general heading of systems analysis we have opportunities to attack the most com-

**Mobile monitors.** Industry must assume the responsibility for the research that will lead to the development of improved sensing and monitoring techniques and hardware for what is a rapidly expanding market. Already, industry has taken some steps in this direction with such devices as the mobile unit (right) that uses a condensation nuclei counter for measuring trace atmospheric gases and particulates or the specially outfitted truck (bottom) equipped to trace and calculate the directions in which smoke and soot travel



plex problems through a three-stage process:

- An exhaustive collection and organization of data pertinent to the problem.
- A mathematical description of the interrelationships discovered, based on the data collected.
- A mathematical optimization, showing the best possible system.

A worthwhile community water-management system, for example, will have complexities which far exceed the capability of old-fashioned trial-and-error methods. It will be necessary to take into account not only the immediate technical accomplishment of a venture, but also the economics, future growth, reliability, maintenance, public acceptance, and many other community parameters. The aerospace industry uses a computerized approach to consider simultaneously millions of

combinations of trajectories, weight, thrust, single- and multistage booster arrangements, vehicle configurations, and the like. The same kind of approach is now beginning to be applied to water-management problems. These certainly can and will be expanded to include a variety of other situations now affecting our environment.

*Improved energy conversion and energy storage systems.* The U.S. Public Health Service has pointed out that of the 133 million tons of aerial garbage dumped into the nation's atmosphere each year, an estimated 85 million tons—almost two thirds of the total—come from sources under the general heading of transportation. I have already mentioned our lack of definitive knowledge about which contaminants cause the most harm. Therefore, it may not be fair to say that two thirds of our air problems come from the internal combustion engine. However, in any case,

it is safe to say that this engine—the most-engineered product in human history—is a major problem as well as being a key factor in our economy and our entire way of living. (Incidentally, this is not just a problem in the crammed United States. For example, the World Health Organization reports that no fewer than 50% of the motorists in Paris are “on the threshold of intoxication”—not from wine, but from carbon monoxide.) One possible solution to the problem of the internal-combustion engine is, of course, to keep on improving it, with greater emphasis on more complete combustion and cleaner exhausts. You are familiar with efforts in this direction, although it is generally acknowledged that even with the best of luck it may be possible only to keep the present situation from getting worse. In the long run, I believe we must look toward other ways to convert chemical—or other kinds of energy—into mechanical energy.

The fuel cell is a device that converts chemical energy directly into electrical energy, without moving parts and with inherently high efficiency, since it does not have the Carnot-cycle limitations which put a ceiling on the efficiency of ordinary heat engines. The fuel cell was invented in England, way back in 1839, but it did not have its first practical application until just short of two years ago in the Gemini V spaceflight. By practical application, I mean that this was the first time a fuel cell was used because it was the best way to do the job. No other power-generating system could have given the 14-day Gemini flight the on-board electric power it needed without exceeding the weight limitations.

Equipment used for space flight is not inexpensive, and the success of fuel cells on the Gemini flights hardly means they are ready for automobiles or trucks. At present costs, fuel cell automobiles are economically out of the question.

However, we should not overlook the pace of recent progress in fuel cell research. For more than a hundred years there was only spasmodic interest in fuel cells, and virtually no scientific progress. But in the past decade all this has changed. Now there are literally thousands of scientists and engineers around the world working on fuel cell technology. The basic type of fuel cell on which the Gemini system is based was invented only about a dozen years ago. Since then, a very great deal has



**Fuel cell.** *The conversion of chemical energy directly into electrical energy in a fuel cell offers highly efficient operations in the absence of noxious fume emissions. This fuel cell operates at moderate temperatures and uses a broad range of hydrocarbon fuels which it combines with air to generate the electricity turning the motor at right. At G.E.'s R&D center, Dr. Leonard Niedrach (left) observes as Dr. Thomas Grubb pours diesel oil into the cell*

been learned, especially as government-funded programs have accelerated the pace of research and development. If the pace of discovery continues, we must consider that in the long run the fuel cell may be a major source of portable power.

Fuel cells have a number of inherent advantages. First, they have high theoretical efficiency, which could mean conservation of fuel resources. They are quiet. Most important, from the standpoint of pollution abatement, it is conceivable that fuel cells can be developed that will have no noxious ex-

haust at all. In the laboratory, fuel cells have been operated, at moderate temperatures, using ordinary hydrocarbon fuels such as natural gas and diesel oil. The scientifically astonishing thing about these cells is that in some types the reaction of the fuels with oxygen from the air goes “all the way”: nothing is left except clean water, harmless carbon dioxide such as that which we all exhale when we breathe, and electricity. It remains to be seen, of course, whether complete fuel cell systems can be developed that will be “completely pure,” but research has shown that such





**Solids.** *Research must lead to a total recovery and recycle of solid wastes as its ultimate goal*

a result is at least within the realm of technical possibility.

What are the problems with fuel cells? There are a variety of problems in addition to the obvious one: They now cost too much. One of the reasons for the high cost is that many otherwise-attractive cells require extensive use of precious metals—such as platinum—in the electrodes. Some of the most efficient fuel cells work only with hydrogen as a fuel, and although there is plenty of hydrogen in the world

(very tightly tied to oxygen), hydrogen is an expensive fuel and likely will remain so for a long time. Then there is the matter of weight and size—present fuel cells tend to take up more space than we would like.

Let us consider the question: “When will we have fuel cell automobiles?” I for one don’t know when, and I’m not really sure if. All I can say on this score is that on the basis of what we know now, fuel cells might someday be very attractive for vehicles because they might not give off any appreciable noxious exhaust, and they might be developed to fit into more compact portable packages, and they might be made inexpensively enough for general use in vehicles.

That’s a mighty long list of “mights.” But fuel cell research has great momentum. The need for alleviating pollution from vehicles is very great. The accomplishments of man, when he puts his mind to it, are being dramatically demonstrated in today’s world.

I can’t promise or guarantee that we’ll all be driving a fuel cell car. But I can assure you that in our own company we feel that fuel cells are extremely promising for both long-range research and more immediate development work. We’re spending a lot of our own money on it, and I don’t hesitate to recommend fuel cell research and development to others—including a continuation of support by the Federal Government.

Incidentally, we should not let the glamor and potential of fuel-cell research cause us to overlook the tremendous opportunities for improving electrical storage batteries. There are few greater challenges for researchers today than the discovery and development of better ways to store electrical energy. An improvement in the efficiency, weight, and cost of storage batteries could have substantial impact on electric vehicular transportation long before fuel cells.

Battery-operated vehicles would be extremely “clean” themselves, of course, but we must remember that we will have a net gain in the fight against pollution from battery-operated vehicles only to the extent that methods which provide energy to charge the batteries are not themselves contributing to pollution. I shall have some comments on this in a few moments, but first let me continue with some other areas

of technology where I think there are important research opportunities.

*Water treatment.* There is no shortage of ideas in this area. Almost any scientist or engineer worth his salt probably can suggest a novel approach to the cleaning or desalination of water. Finding economic solutions is quite another matter. However, I am quite optimistic that intensified effort will produce significant results in the near future. Of utmost importance here, I believe, is that we view the various clean-water problems in proper perspective. Pre-use cleaning and after-use cleaning of water are two substantially different subjects, and there also is a considerable difference between the problems of industrial waste and community waste. Each of these is different technologically as well as economically. A wide variety of solutions will be required.

*Air cleaning.* Also, of course, there is a difference between air conditioning and air cleaning. We believe that new ideas in the electrostatic precipitation of particles, and for removing other contaminants from air, in combination with more conventional air conditioning, can add to the human comforts now achieved by cooling the inside of buildings. We need to clean the air in which we live—starting with those small volumes of air contained in our homes, factories, and offices. To satisfy this need, intensive research is being conducted on permeable membranes that can remove waste gases while—at the same time—returning oxygen to the inhabitants of the building. At best, however, such interior air-cleaning is only an intermediate step toward the ultimate objective of keeping the outside air clean. But, even as an intermediate step, it is important enough to demand further attention in the nation’s laboratories.

*Pollution from insect control methods.* Without getting into that argument about changing the balance of nature, I should like to point out that chemistry is such a versatile and adaptable science that an intensified effort in insect-control research should permit us, in effect, to have our cake and eat it, too. A recent example of a successful chemical effort to eliminate the bad while keeping the good was the solving of the detergent problem: using new chemistry to create the new soft detergents without in any way diminishing their unique cleaning powers. I have every confidence



that, with sufficient research effort, it will be possible to improve substantially our health environment through improved soft insecticides and alternative methods of insect control—and without frightening anyone except, possibly, the insects.

*Sewage disposal.* One of the most intriguing ideas stemming from recent research in microbiology is the prospect of using biological processes to convert domestic sewage into two valuable products: water pure enough for drinking, and a high-protein feed for animals. As we have noted, the simple objective of producing clean water is, of itself, a sufficient motivation for extensive industrial research effort. When the added incentive of producing a profitable by-product is considered, there is every reason to undertake the extensive fundamental research that must be accomplished before this prospect becomes practical reality.

*Solid waste disposal research.* Discarded automobiles, household garbage, and the like produce a problem that cannot be overlooked indefinitely without causing permanent damage to our environment. Society has the responsibility of ridding itself of these waste materials, whereas industry, in addition, carries the burden of minimizing their occurrence. Research must lead to the total recovery and recycle of these wastes as its ultimate goal. Large-scale facilities on community and urban levels need to be developed to process a wide variety of substances in an economic manner.

*Combustion research.* Unburned fuels are part of our aerial garbage, along with unwanted combustion products. I have mentioned the current efforts to improve internal combustion engines themselves. We should also note the opportunity in the area of altering and improving the fuels used, not only in automobiles but also in power plants and countless other industrial and domestic coal- and oil-burning sources of combustion pollutants. New knowledge about basic combustion processes is giving us new hope for simultaneously improving efficiency and reducing unwanted effluents.

In our own company, of course, we are highly interested in central-station electric power generating plants of all types: hydro, fossil fuel, and nuclear. Although we do not manufacture the part of the equipment in a coal-burning

station which involves combustion products, as major contributors to the total station—through turbines and generators and other equipment—we are naturally concerned about alleviating the pollution-potential of the total system (which may be more of a problem in some areas than in others). Thus we have been actively engaged in combustion research for many years, and we are actively seeking ways to reduce unwanted effluents from the fossil-fuel plants which are the mainstay of today's electric power system in this country. These problems are extremely difficult and complex; much progress has been made over the years, and recently built stations are far superior to older power plants. Additional progress should be possible, but the economic consequence of applying technically feasible ideas for removing combustion by-products must not be underestimated.

It is only natural, when faced with the problems inherent in fossil fuels, to think about other energy sources. Hydroelectric power is wonderfully clean, although there are sometimes differences of opinion about the environmental aspects of building dams, regardless of the cleanliness of the electric generating process involved. Although hydro is not the whole answer by any means, because of limitations in suitable hydro sites, there still remain a significant number of opportunities to install more hydroelectric generation facilities in the U.S.—and in a manner supporting the objectives of conservationists.

But the matter of greatest interest to those worried about pollution is the news about nuclear power. First of all, economic nuclear power has come of age much quicker than earlier predictions. Nuclear stations are being installed at a rate far ahead of even the most optimistic predictions of a few years ago. It is difficult to overstate the scope and importance of the revolution in power generation we are experiencing right now.

The nuclear news is especially interesting for those concerned with pollution because the cleanliness of nuclear power plants also has exceeded expectations. There are, of course, no combustion products at all. And the amount of radioactive material emanating from these plants is so small that it is even less than the tiny amounts of radioactive waste emitted by conven-

tional coal-burning power plants as the result of radionuclides occurring naturally in coal.

Certainly, there are many additional opportunities for research to help improve our environment. Those I have mentioned seem particularly important to me because I am aware of research progress in all of them. Success in many of them—if not all of them—seems inevitable.

But although I am aware of progress in these areas, I am not at all satisfied that enough research is being done in any of them. Which brings us to those two difficult questions: Who is going to do it? And who is going to pay for it?

These are difficult questions. Considering the amount of attention that has been directed to them, it is obvious that if they were easy we would have had answers long ago. I should like to make some comments on these questions, but I certainly do not want to suggest that I have all the answers.

It may be helpful to divide the kinds of research opportunities I have been discussing into a smaller number of classifications. We need research aimed at giving us better ways to find out what pollutants are in the air and water and when and how they got there. We need research aimed at learning the effects of these pollutants, especially on people. We need research aimed at keeping certain pollutants out of our environment in the first place. We need research aimed at removing pollutants from our environment.

Research in these classifications of monitoring, causes, effects, preventive regulation, preventive technology, and removal can be further consolidated, for purposes of this discussion, into two categories:

- Research that will produce information useful for establishing standards, determining necessary regulations, enacting appropriate laws, and suggesting methods.
- Research that will produce information useful in developing hardware and systems that can be manufactured and sold.

In the first category is much of the needed exploration about the causes, effects, and preventive regulation of pollution.

In the second category is most of the research that should be done in the areas

of improved sensing and monitoring techniques, prevention systems and devices, and methods of removing pollutants that can't be kept out of the air and water in the first place.

Government, university, and industrial laboratories can all contribute in all of these areas. But it might seem logical to assign the bulk of responsibility in the first category to the Government, since much of it concerns very large-scale public health matters, since it is going to be more effective for the Government to coordinate and conduct many of the massive experiments involving large areas and large numbers of people, and since the initial predominant impact of this part of the work will be, by the definition I have used, on the establishment of necessary laws, regulations, and recommendations.

Obviously, university laboratories (with government support) can make important contributions in much of this work.

In spite of the Government's basic responsibility in this category of the work, the special skills of industrial research can be extremely helpful. Further, the early involvement of industry in all aspects of the pollution problem is essential to pave the way for prompt action once the goals have been set. And, of course, since private industry wants to contribute its knowledge and viewpoints about proposed regulations to combat pollution (especially in regard to the technological and economic feasibility of such proposals), the early and continued involvement of industrial research should be helpful to all concerned.

Industry itself should assume the major responsibility for the research which will lead to hardware and systems needed to monitor pollutants, plus that related to the technology of prevention and removal. The market for sensing and monitoring equipment should grow substantially in the near future, and I believe industry will be missing an opportunity if it does not substantially increase its research effort here at once. (I know one company that is increasing its effort.) In the area of technology for prevention and removal, industry probably will not be motivated to a truly large-scale effort until the monitoring, causes, and effects research makes it possible to identify the guilty pollutants and quantify the objectives in removing them.

Thus, Government will have to carry proportionately more of the research burden in the early stages of this fight than in the latter stages. Once the necessary rules, objectives, and timetables are established, industry will know better how to channel its efforts. But even as this is being done, and even as the problems are being defined, we should continually remind ourselves that the most desirable eventual solutions will come most rapidly if attacked on a competitive basis. The most economic solutions will be diligently sought by private enterprise, and a profit incentive for those who learn how to do the job best will produce the desired results far quicker than any other approach.

As to who will pay for this research, the same sort of pattern seems appropriate. Industry has opportunities it should explore with its own funds in helping develop the kind of monitoring techniques that obviously are needed now. Similarly, industry should be willing to invest more—right now—in the areas of prevention and removal technology where there is no doubt of the eventual need.

But the big surge in industrial research expenditures probably cannot be

expected until the needed "ground rules" are better established. Thus we would look forward to a pattern of increased research expenditure by both government and industry, with the early predominant role of government tapering off and industry's contribution rising rapidly as the objectives become clearly defined.

I assure you that the company I represent has been and is deeply concerned with the technology of pollution abatement. We have tried to take the lead in doing things—frequently very expensive things—that are the responsibility of good corporate citizens in the communities across the nation where we work and live. Similarly, we have devoted a substantial research effort to many areas of technology relating directly to the pollution problem, and we are constantly increasing these efforts. We think it is just plain good business to do these things.

I assure you that we will study the findings of this committee with great care, and we will work vigorously on behalf of making the best contributions we can toward improving the quality of life by protecting and improving the environment in which we work and live.

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*Dr. Arthur M. Bueche is vice president in charge of the G.E. Research and Development Center, Schenectady, N.Y. Dr. Bueche was elected to his present assignment in 1965, when the G.E. Research Laboratory and the Advanced Technology Laboratories were combined into a single organization. He received his B.S. in chemistry from the University of Michigan in 1943, attended Ohio State University, and received his Ph.D. in physical chemistry from Cornell University in 1947. After serving as a research associate at Cornell for three years, he joined the staff of the G.E. research laboratory in 1950. He was appointed manager of polymer and interface studies in 1953 and manager of chemistry research in 1961.*

*Dr. Bueche is known for his work on the physics and chemistry of polymers and the effects of high-energy radiation on plastic materials. At G.E. he contributed to the success of many scientific projects ranging from improved synthetic diamonds to selective membranes, and from new fuel cells to a basic chemical technique called oxidative coupling. The author of many technical papers and holder of a variety of patents, he is also a member of the Board of Directors of the American Chemical Society and has held numerous other ACS posts, including chairmanship of the Kendall Award Symposium (1957), vice-chairmanship of the Division of Polymer Chemistry (1962), and chairmanship of that division (1963). He is a fellow of the American Physical Society (1963) and a member and past chairman of the executive committee of the division of high polymer physics. Dr. Bueche also serves as chairman-elect of the board of trustees of the Gordon Research Conferences and has held other posts within that organization. In addition to his other activities in many scientific organizations, Dr. Bueche includes membership in such scientific and honorary societies as the National Society of Professional Engineers, AAAS, Alpha Chi Sigma, Gamma Alpha, Phi Kappa Phi, Phi Lambda Upsilon, Sigma Xi, and ACS.*

# SMOG SIGNALS

By almost any measure—words, meetings, appropriations,  
scientific and political activities—  
the public awareness and willingness to act on  
the ubiquitous pollution problem  
is rising at a rapidly increasing rate

The smog signals of pollution are being received and read, although not too clearly, in all parts of the nation. The quickening pace of growing interest and action—to say nothing of words—in pollution matters was in marked evidence as 1966 drew to a close.

During the last few days of the year, some 8000 scientists gathered in Washington, D.C., to participate in the annual AAAS meeting whose theme was *How Man Has Changed His Planet*. Earlier in the month the American Institute of Chemical Engineers at their annual meeting in Detroit tackled the problems of water resources in a week-long symposium. That same week industrial managers, government officials, and academicians gathered at Notre Dame to talk about sharing the costs of air and water pollution control.

The week following, the National Industrial Conference Board convened a one-day session on pollution in New York and found its planned conference facilities severely overtaxed as close to 500 industry managers gathered to learn and empathize on the problems of pollution. The next week HEW called a three-day national conference on air pollution whose theme *Control Now for Clean Air* dominated, in subject matter and in the form of two-foot high letters, the 3000-seat main meeting hall. These, and other meetings all over the nation, point to an increasing awareness and concern at all levels and in all quarters about the quality of our environment.

At the HEW meeting, dramatically throwing away his prepared text, Secretary of Interior Stewart Udall summed

up the attitudes as well as anyone: "In past decades we have overemphasized the value of a high-energy society versus a livable society and have accepted a polluted environment as the price we must pay for industrial progress," he said. "Now we realize that with more effort we can have both a clean environment and a highly industrialized economy. Furthermore, it is now clear that the public is willing to pay to achieve this goal. The best evidence of these facts is that smart politicians now are all in favor of a clean environment." The HEW conference served largely to draw together local, state, and national public officials, industry and academic leaders, scientists, and engineers to reason together on the subject of air pollution controls. Most of the talks were reviews couched either in generalities or else in the specifics of what a single industry, research institute, or jurisdiction had done or was planning to do.

Much of the data were not new to those who have been deeply involved in the field. But for those who are concerned with narrow sectors, the program served to round out their knowledge of what is happening on the broad front of environmental management and control.

No immediate results of consequence were evident at the close of the three-day session. But none were expected. As usual in such a meeting, the best that could be hoped for was a broad exchange of information on short- and long-range needs, on existing science and technology, and on the directions in which governmental agen-

cies and Congress might proceed. If the meeting could be said to have accomplished anything, it was to emphasize the political aspects of the problem and the political motivations that will be made obvious in the coming years.

## Political signposts

"The word is 'Go'." That's the way Dr. William H. Stewart, surgeon general, U.S. Public Health Service, summarized the Third National Conference on Air Pollution. "Let's get with it," said Vice-President Hubert Humphrey at the same meeting. "Unless we put a brake on air pollution, air pollution will put a brake on progress," said Dr. John W. Gardner, Secretary of Health, Education and Welfare. "The American people are not really concerned about the source or the composition of dirty air. They want clean air," said Senator Edmund Muskie (D.-Maine). If there had been any doubts about the *Control Now* theme of the HEW conference in Washington in mid-December, speaker after speaker took pains to erase them.

Disclaiming any personal responsibility for the smog emergency during the Thanksgiving holidays in New York City when the city had to shut down incinerators and cease disposal of solid wastes, Dr. Gardner nevertheless admitted the dramatic effect that the smog emergency had on the opening of the HEW conference. The episode was frightening, Dr. Gardner said, but mercifully the pall lifted before drastic measures were called for or before hundreds of lives were lost.



World Wide Photos

*Dim view. Smog emergency in New York City during Thanksgiving holiday set the stage dramatically for the HEW conference*

contemplate. We can wait and court disaster, or take action to clean the air, Dr. Gardner concluded.

### **Changing attitudes**

Evidence that industry is going through a major attitude transition concerning its effluents abounded last month at a National Industrial Conference Board meeting in New York on management of pollution. At the meeting attended by almost 500 industrial managers, NICB released results of a survey of its members, showing that most of the companies contributing to pollution have made its abatement a major corporate concern. Programs have been established, and responsibility for action has been assigned. But the rate at which the companies act and the extent to which corporate funds can be committed for abatement equipment are by no means uniform.

Some companies, for example, try to calculate as a return on pollution abatement equipment an estimate of money saved because of lower accident rates, fewer pollution incidents, and improved community relations—in addition to the more concrete data on value of recovered pollutants. Others figure only on the basis of the value of recovered pollutants. All point out, however, that except for some highly specific instances, money spent on pollution abatement is money spent inefficiently, at least in terms of return on investment as compared with other types of investment.

The justification for spending money on pollution is, therefore, on a more subjective basis and open to a wider

A shroud of pollution blankets the East Coast from Norfolk to Boston and threatens major portions of the rest of nation. No metropolitan area in the U.S. is without an air pollution problem. Thus, our choices are narrow, he continued. We can remain indoors and live like moles; we can issue gas masks; we can live in domed cities. Or we can take action to stop fouling the air we breathe, he reasoned.

We are losing ground in our fight against pollution because neither government nor industry has moved forward with the vigor and determination that the solution to this problem requires. Regional programs are virtually nonexistent. Local air pollution programs are limited and ineffective. Annual spending at the local level for pollution control comes to 15 cents per capita, whereas at least 40 cents per capita is probably necessary for an effective local effort, Dr. Gardner noted.

### **Call for action**

However, there is no simple, quick, or painless solution because the technical, economic, and social factors involved are immensely complex. So, he continued, we must move ahead rapidly on two fronts: Apply existing control technology as fully as possible, and find solutions to the technical prob-

lems which are still beyond our knowledge.

There is no question about our need to expand our knowledge in many areas, for example in the control of the sulfur oxides and the unreasonable stenches that pour from the tailpipes of diesel trucks and busses. But it is even more important to apply the knowledge now at hand, across the nation. The battle for pollution control calls for strong federal-state-local partnerships. But their roles and relationships to each other must be worked out better. We must determine what standards need to be adopted by all these jurisdictions and the way in which they can be applied in a uniform and consistent manner, he cautioned.

The purpose of all our activities in the matter of environmental problems is to achieve a humane environment—a benevolent environment in which the individual can live fully, in good health, free of constraints that limit his potential. If our society continues to become less livable as it becomes more affluent, we promise to end up in sumptuous misery, Dr. Gardner noted.

If the problem continues to get worse and if we continue to lose ground until some frightening incident occurs, then we must be prepared for an angry public to call for measures far more rigorous and militant than anything we now

range of interpretations from company to company and industry to industry than most investments. Some organizations approach such spending, in fact, as they do their corporate giving to local charities, education, and other social-benefit projects and programs.

Industry has not yet reached a consensus on the role of the Federal Government and on the methods of interaction between government, industries, and companies. But fear of emotional pressures for "overcontrol" are general, even though few are willing to say how much would be too much.

### Sharing control costs

The headline of a feature article in the *South Bend Tribune* on the evening preceding the Notre Dame conference on sharing the cost of air and water pollution control proclaimed that "Air Pollution Control Is 'Dull' Issue."

Fortunately, at least for the 200 government and industry representatives attending the conference, the newspaper article dealt with local issues. But a line in the lead paragraph touched on something which, though not planned that way, has been a recurring comment throughout many of the conferences on pollution control. "Lack of sufficient information is a problem," the feature writer stated.

Agreeing with this point of view, the lead-off conference speaker, Dr. James J. Flannery, chief economist of the Federal Water Pollution Control Administration, said that there are no satisfactory estimates of the cost of pollution control." All such estimates omit some significant aspect such as land drainage effects, bottom deposits, and industrial waste loads. Knowledge of the magnitudes and costs of the industrial aspects of the problem is most scant," he continued. However, despite general dissatisfaction with present estimates of costs and their probable distribution among governments and industry and their impact on the economy, including effects on public borrowing, interest rates, tax levels, prices, and profits, control actions must continue. The requirement for studies does not suggest further waiting, Dr. Flannery said.

Congress has recognized the deficiency of knowledge in these areas and through the Water Quality Act of 1965 and the Clean Waters Restoration Act of 1966

is seeking a variety of information. To help develop a program to enhance the quality and value of the public waters, Congress has moved in several directions:

- Means were provided to expand and emphasize the traditional programs of study, research, technical assistance, financial assistance, and enforcement.

- A new tool, water quality standards on interstate streams, has been added.

- Reliable figures that include the costs of treating industrial and other wastes as well as municipal wastes must be developed by the Secretary of the Interior by January 1968.

The traditional program will help to give us a sound basis for action. The water quality standards must be reached through public hearing to determine the use and the value of the water involved. A reliable figure for the cost of pollution is essential if a reasonable program of future pollution control requirements is to avoid being disruptive to industry, in particular, or to the economy in general, according to Dr. Flannery.

### Industry's record

Industry may have already invested billions of dollars in pollution control and it may be spending hundreds of millions of dollars per year for operating expenses for pollution control equipment. "Whatever the industry record has been in the past, it has not been good enough, judging by the general condition of the public waters."

Industry is well aware of the significance of the new legislation, the new public attitudes, and the new attention being devoted to pollution problems, Dr. Flannery continued. The public wants more, not only in terms of controls, but in terms of water quality—quality must be enhanced not merely sustained, he noted. This demand means that manufacturing operations must begin to emphasize waste controls—the reduction in volume and strength of the wastes—not their clean-up after they are in the stream.

Despite the growing emphasis on the reduction of waste effluent, there is little present inclination to consider user charges as legislative proposals. Whatever the practicality of user charges, the most promise for pollution control leading to water quality objec-



**James J. Flannery**

*Industry's record not good enough*

tives and a gain for manufacturing efficiency rests with a program that is conducive to waste control and reduction. Waste treatment at the end of the line is not desirable, Dr. Flannery noted. The Clean Waters Restoration Act requires a study of incentives to industry including, but not limited to, tax considerations. But the task is not going to be easy because of the wide disparity in the industrial picture.

Economics is at the core of the federal program to control pollution, Dr. Flannery said, but it is difficult to generalize on the financial effects of pollution control requirements. Yet, the most effective pollution control is obtained by process adjustments and management practices. Thus, government policy should be shaped as a supplementary force to these factors.

### No choice in air pollution

The afternoon sessions at Notre Dame turned to the considerations of the economic aspects of the federal air pollution program. Several alternative courses of action are available to us in dealing with contamination of our environmental resources. For example, the degree of pollution control relative to our water resources depends in large measure on the use we plan to make of the waterway. But no such choice exists in the area of air pollution, said Mr. James A. Anderegg, assistant to the chief, Division of Air Pollution, Public Health Service. "We cannot decide to reserve only a portion of the air resource for breathing; wherever men live and work, they must breathe the air



as it comes to them, contaminated or not.”

We need more information to plan effectively for long-range proper air resource management, he continued. Yet, we know enough to bring about improvement in air quality or to prevent its further deterioration to take action now. Air pollution costs the country billions of dollars a year through injury to vegetation and livestock, corrosion and soiling of materials and structures, depression of property values, and interference with ground and air transportation. Also, we must consider the adverse effects of air pollution on human health both from the acute and long-range exposure effects.

Meanwhile, Mr. Anderegg pointed out, the problem of air pollution is steadily worsening. We have technical means for preventing or minimizing the discharge of most types of contaminants to the atmosphere. For other contaminants for which effective procedures are not now available at socially acceptable costs, current research will probably make new tools available soon. In any event, the average citizen realizes that the development of effective control programs to meet air pollution problems is essentially a social and political decision which rests in his hands, Mr. Anderegg said.

### **Regional approach**

Although creation of new county or city programs is a step in the right direction, it is hardly an adequate response to a problem whose very nature demands that it be attacked on a regional basis in virtually every one of our large urban areas. HEW has initiated formal abatement actions in nine interstate areas, covering parts of 13 states and the District of Columbia. Furthermore, studies are under way in many of the 70 large metropolitan areas which cross or abut state boundary lines.

Nonetheless, before programs can be undertaken in the most effective manner, air quality criteria must be developed. These criteria will enable state and local agencies to set and enforce air quality standards. Already HEW is developing such criteria for the sulfur oxides (from the combustion of sulfur-bearing fuels) and oxidants (products of atmospheric reaction by which motor vehicle pollutant gases are converted to photochemical smog).



**John W. Gardner**

*Pollution can put a brake on progress*

There is good reason, Mr. Anderegg said, to be confident that we can halt the rising sulfur oxide contamination of the atmosphere by using low-sulfur fuels or by desulfurizing certain fuels.

Automotive pollution is an instance of the need for direct control action at the federal level. The relentlessly rising trend in the use of motor vehicles means that control measures must be initiated now to prevent the problem from reaching intolerable proportions. But, said Mr. Anderegg, the motorist buying a 1968 car will probably complain about the cost of a direct charge for air pollution control.

### **Universal responsibility**

No one escapes responsibility for contributing to air pollution. Nor can any of us escape the consequences of a polluted atmosphere. The fact is, Mr. Anderegg pointed out, each member of society will have to pay for abatement and control.

In most instances the cost of controlling air pollution is sufficiently indirect that the citizen does not recognize the charge for what it is. For example, the switch from high- to low-sulfur fuel, recently announced by Consolidated Edison of New York City, may cost \$12 million a year. In terms of the individual consumer, these higher fuel costs mean less than \$1.50 per capita per year, hardly an unreasonable expenditure in the interest of cleaner air, better health, and increased enjoyment and community pride, Mr. Anderegg noted.

What industry has not done is to



**Hubert H. Humphrey**

*Let's get with it*

express its efforts in atmospheric improvement in terms of mills or cents per unit of product output—or even in fractional cents per unit of secondary output such as a car or a book where the primary polluting industry is steel or paper.

We can afford clean air, said Mr. Anderegg. If we consider the relatively high figure of \$850 million per year for installation and operation of equipment, disposal of collected pollutants, and taxes, we can translate these figures to 3% of new plant investment or 0.5% of the value added by manufacture or 0.14% of the gross national product. By any standard, these expenditures do not appear likely to bankrupt the country, Mr. Anderegg stated.

### **Economic and political impediments**

There are two impediments to achieving effective control—economic and political. The economic impediment derives from the fact that for the most part those who contribute to the sources of pollution are not the ones who suffer the effects so that there is little if any economic incentive for the polluters to control pollution. The political impediment derives from the fragmentation of political responsibility.

A regional approach to air pollution control is needed, but, unfortunately, has not materialized in practice. Local governments appear almost universally unwilling to relinquish any jurisdictional authority to a regional organization. Leadership by state government can play an important role in evolving regional programs. If states do not



pick up the challenge, other means will have to be found to obtain the development of the needed regional programs.

"With a growing clamor from the man in the street who pays the bill, there seems to be little reason to delay further the inevitable clean-up process," Mr. Anderegg concluded.

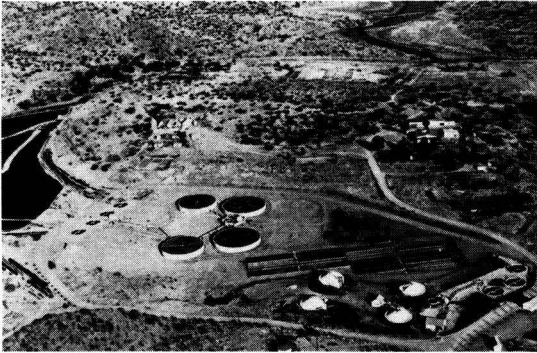
**Chemical engineering survey**

The week-long sessions on water resources at the AIChE meetings in

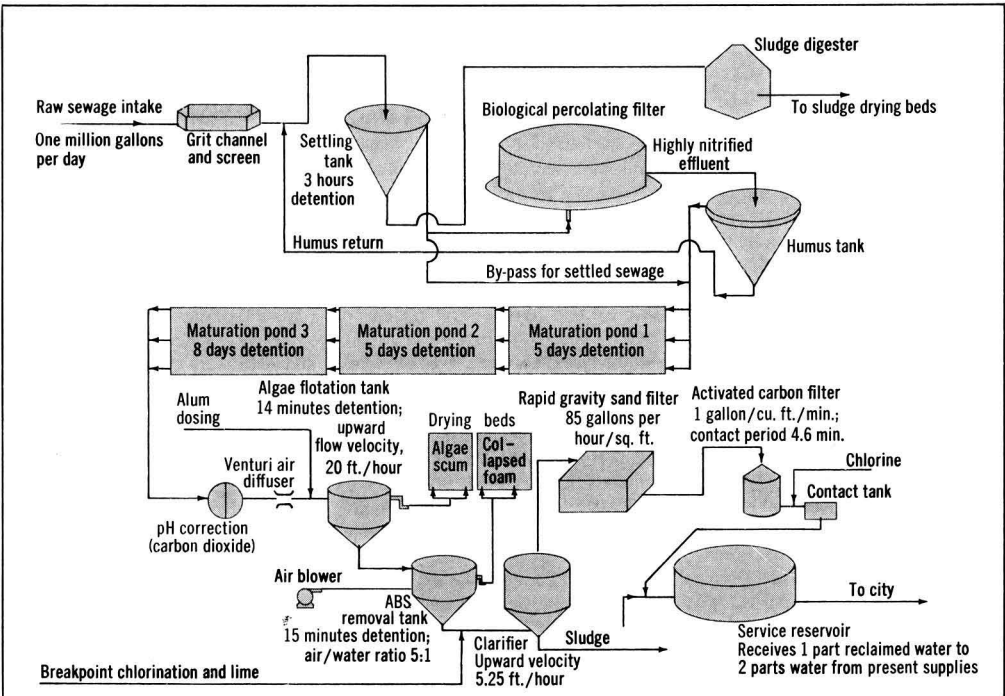
Detroit emphasize the importance of the subject to a large scientific body, which can contribute a great deal to the solution of the problem, nationally and worldwide. Ranging from a discussion of environmental pollution in the Great Lakes region and moving through the discussions of water resources and government policy, a large portion of the symposium was devoted to the subject of water conservation by re-use. Organized by Lawrence K. Cecil, chemical engineering consultant on

waste water and water re-use (Tucson, Ariz.), the sessions were well attended.

Pointing up the value of international exchange of data was a paper given by G. J. Stander and J. W. Funke from the National Institute for Water Research (Pretoria, South Africa). Although Dr. Stander called attention to many industrial efforts to re-use water or to upgrade industrial processes to cut down on industrial needs for water, his reference and discussion to a closed-loop system in which domestic



**Closed-loop sewage / domestic water supply system works in South Africa**



sewage effluent was made available for domestic use was the subject that titulated the conferees.

#### **Closed-loop sewage system**

The closed-loop system supplies the city of Windhoek in South West Africa with water for domestic use. A fully integrated pilot plant, soon to be replaced by a full-scale reclamation plant already under construction and slated for operation early this year, comprises the following four major units:

- A conventional sewage works for what is essentially domestic sewage. The industrial area is provided with separate disposal facilities because its sewage interfered with the effluent quality needed for the domestic recycling.
- A maturation pond system in which algae and planktonic organisms, such as are in evidence in most oxidation ponds, are used to produce a raw water suitable for advanced purification.
- A unit for the bulk removal of plankton (mainly algae), organic material, bacteria, viruses, and synthetic detergents.
- An activated carbon filter for final polishing of the effluent with regard to organic residues, particularly syndets.

#### **Phosphate removal**

Phosphate removal from municipal sewage effluent has been a long-sought goal. Municipal engineers and others interested in solving the problem of high phosphate content in effluent water and the concomitant algal blooms in receiving waters have recently had their hopes raised for a relatively easy solution. Disclosure that a sewage treatment plant in San Antonio, Tex., had an unusually low phosphate-containing effluent had been made more than a year ago.

At the AIChE meeting, however, some specifics of the San Antonio operation were discussed in detail. Don Vacker (superintendent of wastewater treatment plants, San Antonio), Dr. C. H. Connell (professor of environmental health, University of Texas Medical Branch, Galveston), and W. N. Wells (engineer-in-charge of wastewater treatment, San Antonio), discussed their original observations and subsequent test programs.

Of three sewage treatment plants in

the San Antonio area, one had a very low phosphate content in its effluent—close to 90% was removed. Comparison of the operating conditions of the three sewage plants revealed that operational features at the low phosphate plant differed in five major ways from the procedures at the other two plants.

Although all three facilities were secondary waste treatment plants, using an activated sludge process that involves settling and aeration and the use of bacteria to break down and assimilate biological impurities that remain after the settling-out stage, they were found to differ essentially in the following areas: aeration, bacterial concentration, settling time, holding time for settled materials remaining in the settling tank, and the ratio of bacteria to organic materials.

The full details of the significant factors are not yet known, according to the San Antonio workers, but some preliminary conclusions can be drawn. A high degree of phosphate uptake by activated sludge depends on a high level of dissolved oxygen in the aeration tanks. When oxygen levels drop, phosphate is leached from the sludge solids and enters the discharge effluent. A very high rate (nearly complete uptake) of phosphate does not begin until a dissolved oxygen level of close to 2.0 milligrams per liter of oxygen is attained.

If the 2.0-milligram-per-liter dissolved oxygen content is not surpassed in the final one fourth of the aeration tanks, considerable phosphate leaching occurs, probably as a consequence of increased endogenous destruction of cell solids in the aeration tanks.

However, attainment of proper oxygen levels is conditioned by other factors within the sewage treatment system. And, although there is strong evidence that the oxygen level per se is the controlling factor, related factors that affect the attainment of appropriate oxygen levels may also be important. For example, a ratio of maximum to minimum BOD or PO<sub>4</sub> loadings of roughly 4/1 implies that there is sufficient solid building material to take up the phosphate in the system. A higher ratio in which, for example, a high BOD level occurs, leads to additional demands on the system for oxygen build up.

Currently, the San Antonio workers and a task force from the Water Pollution Control Administration are investigating the problem in an attempt to

accelerate the development of maximum removal of phosphates as a regular part of municipal waste treatment.

#### **Man and his planet**

With topics ranging from weather modification, population control, the threat of science to traditional values, physics of the moon, and the scientific aspects of pest control, to such others as biology of the mouth, circadian rhythms, world weather watch, warning phenomena, religion and science, agriculture and the quality of our environment, and pollution control, scientists, educators, and interested laymen gathered for the annual AAAS meeting in Washington. The theme of the meeting, *How Man Has Changed His Planet*, brought together a wide variety of disciplines to attack the problem on many fronts.

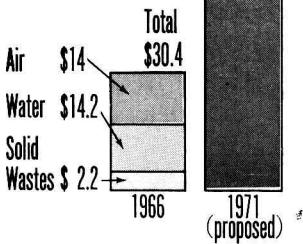
Not the least of these, by measure of interest or attendance, were the sessions devoted to matters of immediate environmental interest.

In his Sigma Xi-Phi Beta Kappa address, Dr. Walter O. Roberts, director of the National Center for Atmospheric Research (Boulder, Colo.), noted the very serious concern of U.S. scientists about environmental pollution. He posed the dichotomy that nearly every advance of science has two faces. "One smiles on us and lifts the aspirations of man; the other scowls sternly on all future hopes." For example, Dr. Roberts continued, the miracle of the modern automobile brings with it the scourge of car-borne air pollution that threatens to choke our large cities. A growing urbanism, made possible by air conditioning and food transportation, brings with it befouled rivers, vanishing privacy, and lives of strain and tension.

The age of technology in which we live brings with it the expectation that we can live in harmonious equilibrium with a natural environment of quality. However, he continued, we must take a vital, flexible, and ever-evolving concern about the nature and purpose of man and about what constitutes a good life in a good society in the light of today's communications, population growth, races, political systems, and weapons. We must plan creatively to shape the new, Dr. Roberts continued. There will always be dangers, he notes, but we must have the courage to put in practice

# Daddario Committee suggests 10-fold increase in federal R&D pollution expenditures

All figures in millions  
Total \$300



Source: House Subcommittee on Science, Research, and Development

the findings that come out, no matter how hard they hit at the patterns of our folkways.

### Man to blame

Continuing with the theme that man has himself to blame for most of our environmental problems, Louis M. Glymph, an administrator of soil and water conservation research in the USDA, and Herbert C. Storey, watershed research in USDA's forest service, observed that erosion and sedimentation, processes as old as the planet itself, have been greatly accelerated by man's exploitation of soil, water, and vegetation. But, the authors noted, proper land management can reduce the sediment load of streams, although some areas of sedimentation research need considerable more effort. For example, the two authors said that we must find ways to determine the worst source of sedimentation, we must develop techniques for finding out how much chemical and industrial waste is carried by sediment, and we must determine the cost of stopping such pollution.

Associated with this concept of sedimentation problems was a paper by Dr. Jacob Verduin, professor of botany, Southern Illinois University. He described some of the relationships between eutrophication and agriculture. Less than half of the phosphorus enrichment on stream and lake waters derives from agricultural fertilizers.

The major portion derives from the effluents from cities and suburbs. The principal source of the phosphorus from cities and suburbs are household detergents. Nonetheless, if we were able to find an adequate and effective substitute for phosphorus in the detergent molecule, phosphorus enrichment of our streams would be reduced by about only one half, a condition still too rich for comfort.

One way to counter the high phosphorus levels, Dr. Verduin noted, would be to build ponds, lagoons, and reservoirs to hold fresh waters longer and delay their movement to the sea. Aquatic communities would thus have time to reduce nutrient levels, particularly the phosphorus levels. But

more research is needed to find aquatic plants that can speed the process of phosphorus removal.

Before meaningful and effective action can be taken to control the levels of unwanted materials in our streams, we must have a better idea of the content of these materials in the water systems as they exist. To this end, many organizations, particularly the plant pest control division of the USDA's agricultural research service, have monitored the pesticide content in water in selected areas throughout the U.S.

On the basis of these measurements, Leo G. K. Iverson, assistant director of USDA's plant pest control division, noted that quick runoff from floods or heavy rains may be responsible for much of the contamination that enters our waters. However, there are other complicating factors such as seasonal factors and the time between chemical application and rainfall.

There seems little doubt that contamination of water by pesticides is directly related to the amount of sediment or other suspended material in the water. The results of many analyses of water samples reveal that neither deep nor shallow wells are currently being contaminated by insecticides when the well is built in a manner that normally provides water fit for human use. On the other hand, water with such suspended material as silt, algae, plankton, or dead organic matter has pesticide residues, although the water itself may, in fact, not contain a measurable amount of pesticide.

The prime function of the USDA's monitoring program is to determine the facts of water contamination and to use these facts to develop corrective action to stabilize and hold pesticides on the target area, Mr. Iverson concluded.

### Safe pest control

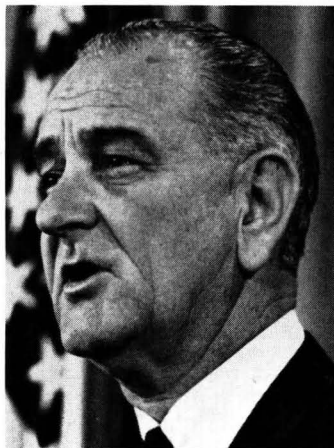
Pest control is essential, said Dr. George L. Mehren, assistant secretary, USDA. Nonetheless, Dr. Mehren noted, the department is aware of the often complex and difficult trade-offs involved in choosing among alternative methods. The department's basic judgments on pest control are made, at least partly, in terms of the depart-

## President Johnson's State of the Union Address

**... We have begun to rescue our waters from the menace of pollution and to restore the beauty of our land. . . We should vastly expand the fight for clean air with a total attack on pollution at its source, and—because air, like water, does not respect man-made boundaries—by setting up "regional airsheds" throughout the country. . . .**

**... We should carry to every corner of the Nation our campaign for a Beautiful America—creating more parks, more seashores, and more open spaces for the generations that come after us. . . .**

Jan. 10, 1967



ment's primary mission—assuring an adequate supply of safe and wholesome food for satisfying domestic needs and for fulfilling the nation's international and other commitments.

There really is no present or even potential prospect of eliminating the need for all pest control, Dr. Mehren continued. USDA, therefore, seeks to develop, promote, and use methods of pest control that are as effective and safe as science can make them. The department supports the use of biological, cultural, and other alternatives to pesticides wherever these means are effective. At the same time, the department recognizes that the needed protection often can be provided by conventional pesticides, safely applied, he said.

The department has convincing evidence that pesticides are being used safely now, as a result of the department's research, regulatory, and educational efforts. There is, for example, no cumulative contamination of the environment when USDA recommendations are followed carefully, Dr. Mehren said.

### Land pollution

One of the most important developments in the field of environmental science has been an awakening to the hazards of land pollution, said F. R. Bowerman of Aerojet-General Corp. There has, until recently, been little

attention paid to the long-lasting effects of pollution of the earth's surface. Now, however, the Federal Government, universities, and technical institutes are developing the technology and instrumentation necessary to the evolution of techniques to prevent degradation of the soil and the ground waters of the nation.

The soil is not a perfect biological incinerator. We have too long accepted the principle of microbial infallibility—the existence of a natural, highly heterogeneous community of microorganisms that will break down any organic substance presented to it. We should not be surprised at this turn of events, said Dr. M. Alexander, professor of soil science, Cornell University.

We are now introducing organic molecules not known to be generated biologically into man's environment, and we can assume that no enzymatic mechanism exists for their degradation. The biological incinerator simply may not be capable of handling all things thrust into it, Dr. Alexander said. And we must recognize this fact.

There is a considerable, but far from complete, body of information on the breakdown of pesticides in soil, he noted. Frequently the agents of inactivation are not known. These agents must be defined and the environmental factors influencing their effectiveness must be determined, if we are to achieve careful control and management of soil pollution.

### Managing environmental quality

In his paper on environmental quality management, Dr. Walter R. Lynn, associate professor of environmental systems engineering and director of the Center for Environmental Quality Management at Cornell, observed that the scope and intensity of man's interaction with his environment are being dramatically altered by changes in the environment. Limited air, land, and water resources must be exploited to support a constantly increasing population concentration while being expected to assimilate the steadily expanding spectrum of wastes being generated and released. Man's environment is being modified to the point where survival of modern industrial society requires that the environment be controlled.

The approach to the modification and control of the environment oriented to limited objectives has, in turn, had limited success because it does not take into account the interdependence of environmental health problems. We need to know not only the elements of pollution control, but also how best to use the available technology and how best to allocate resources in an efficient manner.

In the long run, Dr. Lynn noted, the objective is to provide public policy makers with the tools to manage the environment so as to maximize its beneficial effects on the members of the society.

# A shorter name for high-reliability, portable air samplers ...ENI

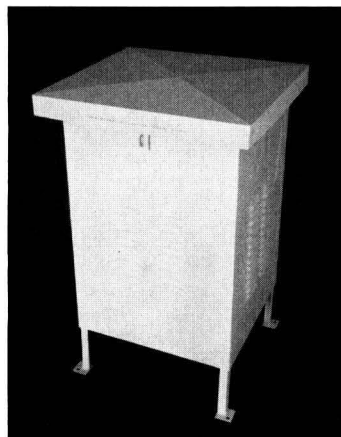
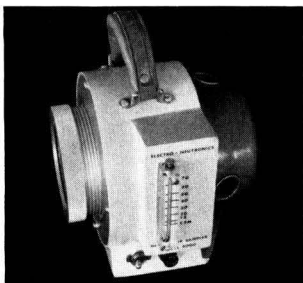
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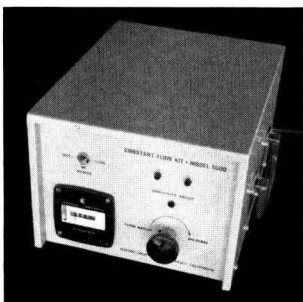


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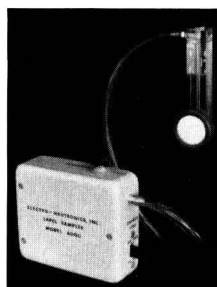
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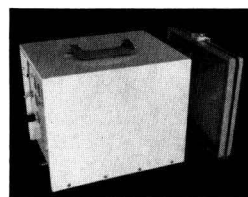
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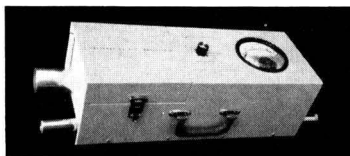
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1. Little, C., Locky, C., Lurkey, T., et al.,  
in English Fairy Tales, David Nutt, London, 1890.

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## Laboratory Method for Predicting Calcium Sulfate Scaling Thresholds

Julius Glater, Louis Ssutu, and Joseph W. McCutchan

Department of Engineering, University of California, Los Angeles, Calif.

■ An experimental method for measuring calcium sulfate scaling thresholds of natural saline water samples at 100° C. is based on visual observation of freshly formed hemihydrate needles from evaporating brine solution. A novel all-glass laboratory evaporator has been developed. The crystal phase was identified as pure calcium sulfate hemihydrate by x-ray diffraction. Critical concentration factors measured for sea water, Roswell brackish water, and Salton Sea water were 3.2, 2.6, and 1.1, respectively. The influence of ionic strength on calcium sulfate solubility is clearly indicated. A graphical method relates scaling threshold to calcium and sulfate ion concentration for a given saline water. This technique should be useful in estimating the calcium sulfate scaling potential of any natural water in a distillation process.

perature and concentration factor) for hemihydrate precipitation from a given saline water.

### *Purpose of Work*

We have devised a rapid experimental method for determining concentration thresholds at which calcium sulfate scale begins to deposit from a saline water sample at its atmospheric boiling point. The method is rapid and easily reproducible by inexperienced personnel. It involves simple laboratory apparatus and small samples of water, and furthermore avoids the necessity of long runs in commercial distilling equipment.

Many recent studies on equilibrium solubility of calcium sulfate appear in the literature (Dickson *et al.*, 1963; Marshall *et al.*, 1964; Power *et al.*, 1964). These reports are based largely on solubility in pure water or solutions of sodium chloride. Solubility data obtained from distilled water or dilute salt solutions cannot be applied directly to sea water, a complex system of mixed electrolytes. For example, the solubility of certain sparingly soluble salts may be increased as much as three times in 0.1M salt solutions of monovalent type and ten times in 0.1M solutions of divalent type. It is therefore difficult to predict equilibrium solubilities in sea water (about 0.5M in NaCl) from data obtained from simple solutions. Fundamental work on hemihydrate solubility in natural sea water has been reported by Langelier *et al.* (1950) and Toriumi *et al.* (1933). The Langelier study gives a threshold concentration factor of 3.1 for deposition of calcium sulfate scale at 100° C. Calculations by York and Schorle (1966) based on Toriumi's data agree closely with the Langelier value.

Concentration factor (CF) is a frequently misunderstood term in engineering literature. It may be defined as the ratio of salinities of blowdown to feed water for an evaporator. In a batch distillation process, concentration factor is defined as follows:

$$CF = \frac{\text{initial volume of saline water}}{\text{volume of residual brine}}$$

Table I shows the relationship between concentration factor and other common units for expressing sea water concentration. Langelier's value of 3.1 has been used widely for calculation of safe blowdown ratios in various types of distilling equipment. Unfortunately, the Langelier work was done in sea water at 60° and 100° C. only. Several important questions on calcium sulfate precipitation threshold still remain to be answered.

The deposition of mineral scale from evaporating brine solutions poses a serious problem in the development of reliable and economical equipment for saline water distillation. Technology of alkaline scale control has been substantially advanced during the past few years, but calcium sulfate deposition remains as a potential problem. Alkaline scale, consisting of calcium carbonate and magnesium hydroxide, is formed by reactions resulting from the thermal breakdown of bicarbonate ion which occurs in all natural saline waters. Bicarbonate ion can be effectively decomposed by injecting a low concentration of strong acid into evaporator feed water. Acid injection followed by deaeration has been used successfully for control of alkaline scale in many large distilling plants (Checkovich, 1964; Mulford *et al.*, 1965).

Calcium sulfate scale is precipitated when the equilibrium solubility of a given crystalline form of this compound is exceeded. This occurs when certain saline waters are concentrated by distillation. Although anhydrite (CaSO<sub>4</sub>) is the most stable crystalline modification at usual evaporator temperatures, the somewhat more soluble hemihydrate (CaSO<sub>4</sub> · 1/2H<sub>2</sub>O) precipitates first and is found most frequently in actual scale samples, because of the long time required (approximately 17 hours at 100° C.) before any hemihydrate converts to the more stable anhydrite form. That the solubility of calcium sulfate is also strongly influenced by temperature can be seen from the steeply inverted solubility-temperature relationship of these two scale modifications. In distillation processes we are therefore concerned with critical conditions tem-

**Table I. Sea Water Concentration Units**

Concn. Factor	% Distilled Water	% Brine	% Increase in Concn.	% Total Dissolved Salts	Salinity
1.0	0.0	0.0	0	3.50	35.0
1.1	9.0	91.0	10	3.85	38.5
1.2	17.0	83.0	20	4.20	42.0
1.5	33.0	67.0	50	5.25	52.5
2.0	50.0	50.0	100	7.00	70.0
2.5	60.0	40.0	150	8.75	87.5
3.0	67.0	33.0	200	10.50	105.0
3.5	71.5	28.5	250	12.00	120.0
4.0	75.0	25.0	300	14.00	140.0
4.5	77.8	22.2	350	15.75	157.5
5.0	80.0	20.0	400	17.50	175.0

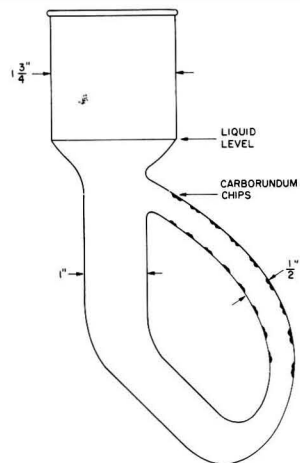


Figure 1. Modified Thiele tube

1. What is the scaling threshold of sea water samples at different dilutions? For example, how can one experimentally evaluate the scaling potential of waters from bays or coastal regions near rivers?

2. What is the scaling threshold of natural saline waters with different ionic distributions than sea water?

3. How effective are various water pretreatment procedures for control of calcium sulfate scale? For example, how can one experimentally evaluate the scaling potential of waters treated with precipitating agents, complexing agents, or ion exchange resins?

4. What is the scaling threshold of natural waters at distillation temperatures above 100° C.?

This work describes an accelerated experimental method for providing answers to questions 1 through 3. By the technique proposed here, it is possible to set design limitations for preventing calcium sulfate scale in an idealized distillation process and to gather data for any saline water sample distilled at 100° C. The method is based on conditions approaching equilibrium between solid hemihydrate and its dissolved ions. In actual distillation practice, attainment of equilibrium is not always possible and some variation between different types of distilling equipment may be noted. Sea water data collected thus far are in good agreement with Langelier.

This series of experiments was carried out at the atmospheric boiling point only. The effect of temperatures above 100° C. on calcium sulfate solubility in sea water has not been rigorously studied. Hemihydrate curves relating sea water concentration factor with temperatures up to 300° F. have been drawn from limited experimental and operational data (Skerritt and Howe, 1966; Standiford and Sinek, 1961). The exact position of these curves is controversial and provides no clear limit for prediction of scale-free operation in distilling plants. We are currently applying our technique at higher temperature levels in an effort to provide additional data on the solubility of hemihydrate in sea water.

#### Apparatus and Experimental Procedure

Boiling water containing dissolved calcium and sulfate ions will immediately deposit hemihydrate crystals upon reaching

the saturation point. Observance of this phenomenon suggested the possibility of devising a visual method for detecting the first appearance of hemihydrate crystals in evaporating brine solutions. Natural sea water obtained from Marineland in Los Angeles was first acidified with hydrochloric acid to a methyl orange end point (pH 4.0) in order to prevent the formation of alkaline scale. The acidified water was then evaporated slowly to CF  $\cong$  2.0. A portion of this preconcentrated water was placed in a small beaker containing a glass immersion heater and evaporation was continued. It was anticipated that crystals would appear on the immersion heater at the point of saturation. As the brine became more concentrated, however, violent bumping was observed. Bumping was not improved with boiling chips but could be avoided by stirring rapidly with a magnetic stirrer. Turbulence in the solution caused crystals to flake off the heat transfer surface as soon as they formed. The resulting slurry of fine needles developed slowly after saturation was achieved. No definite saturation end point could be observed in the rapidly moving solution. Attempts to improve this system were ultimately abandoned in favor of a more efficient glass evaporator.

A device was finally developed based on the Thiele-Dennis tube (Dennis, 1920) commonly used for melting point baths in organic chemistry laboratory, modified as shown in Figure 1. The wide neck was added to enhance evaporation from the liquid surface and to provide a surge volume in case of bumping. Carborundum chips sealed into the narrow arm facilitate more even boiling and promote nucleation of calcium sulfate crystals. The Thiele tube configuration enhances natural brine circulation at a fairly slow rate. This geometry together with Carborundum chips at the point of heat input ensures even boiling with no bumping observed.

To determine the critical concentration factor for hemihydrate deposition in sea water, the following procedure is followed: About 3 liters of acidified sea water (pH 4.0) is evaporated slowly on a hot plate with stirring to a concentration factor about 0.5 CF unit lower than the anticipated critical concentration factor. The preconcentrated solution is now filtered by first stirring in 50 grams of Celite and transferring the milky suspension to a fine sintered glass vacuum filter.

It is very important to remove small suspended particles from the preconcentrated brine, since this method is based on a visual end point observed under magnification. Even small traces of solid impurity may interfere. The Thiele tube is filled to the indicated mark with a measured volume of brine filtrate. Another portion of filtrate is used to fill a 50-ml. buret. The apparatus is now assembled as shown in Figure 2, with heat applied to the narrow arm through heating tape connected to a Variac. The power input is adjusted to produce gentle boiling and brine circulation. Water vapor is discharged directly into the air as evaporation proceeds, and a constant liquid level in the Thiele tube is maintained by slow addition of fresh filtrate from the buret.

When boiling brine becomes saturated with calcium sulfate, a slurry of fine crystal needles suddenly appears in the body of the circulating fluid. These probably form on the Carborundum chips first and are then dislodged by the fast-flowing brine stream in the narrow arm. The end point at which crystals first appear can be observed in a darkened room by using a 10X hand lens or small telescope. The visual field is illuminated by a high intensity light source placed at about 90° to the line of sight. Observations are made in the wide arm of the tube, where liquid circulation rate is slow.

End point detection may be substantially improved by using plane-polarized light in place of ordinary light. Polarized light has been used by Gross (1954) for detection of sodium chloride crystals from biological fluids. Apparatus shown in Figure 3 must be arranged so that telescope, large arm of Thiele tube, and light source are oriented in a straight line. A piece of Polaroid glass is placed between the tube and light source and another piece between the tube and telescope. The two polarizers are oriented at 90° to one another, so that a dark field is observed. Polarized light passing through a water sample will be stopped by the polarizer placed at right angles to the plane of polarization. When small crystals appear in the water, light will be refracted from these crystals in such a manner as to alter the plane of polarization. Some of the refracted rays will now pass through the second polarizer. Small crystals appear as bright points of light on a dark field. This modification gives sharper end points and has improved the precision of these measurements. Vapor bubbles do not refract polarized light and appear transparent in this system.

At the completion of each run, the Thiele tube is filled with distilled water, heated to the boiling point for a few minutes, then rinsed with fresh distilled water and placed in a glass drying oven overnight. If tubes are not cleaned in this manner, the Carborundum chips become fouled with brine or salt crystals and violent bumping will result in subsequent runs.

#### Calculations

When the end point is reached, power is turned off and the Thiele tube is cooled to room temperature. A buret reading is taken and the volume of added filtrate recorded. The volume of concentrated brine in the Thiele tube is measured by transferring the cool contents to a graduated cylinder. Although the evaporation is carried out at constant liquid volume, there is usually a small discrepancy between the initial and final Thiele tube volumes. Concentration factor may be calculated from the following relationship:

$$CF = \frac{(V_i + V_b)CF_p}{V_f}$$

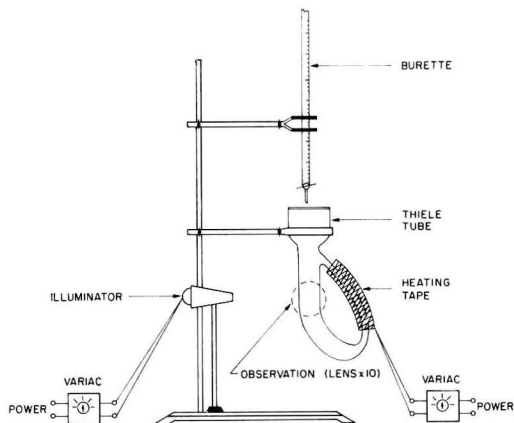


Figure 2. Experimental apparatus using ordinary light

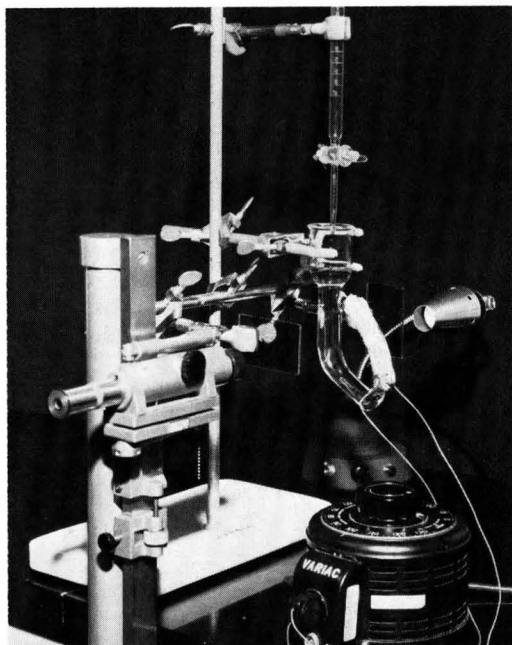


Figure 3. Experimental apparatus using polarized light

**Table II. Analytical Data on Three Saline Water Samples**

Source of Saline Water	Ca <sup>+2</sup> Concn.	SO <sub>4</sub> <sup>-2</sup> Concn.	CaSO <sub>4</sub> Ion Product	Critical CF
Sea water, Marineland, Calif.	400 p.p.m.	2600 p.p.m.	$2.71 \times 10^{-4}$	3.18
	$1.00 \times 10^{-2} M/l.$	$2.71 \times 10^{-2} M/l.$		3.16
				3.19
Brackish water, Roswell, N. M.	488 p.p.m.	1510 p.p.m.	$1.93 \times 10^{-4}$	2.61
	$1.22 \times 10^{-2} M/l.$	$1.58 \times 10^{-2} M/l.$		2.58
				2.60
Saline water, Salton Sea, Calif.	616 p.p.m.	7260 p.p.m.	$1.17 \times 10^{-3}$	1.10
	$1.54 \times 10^{-2} M/l.$	$7.56 \times 10^{-2} M/l.$		1.10
				1.13

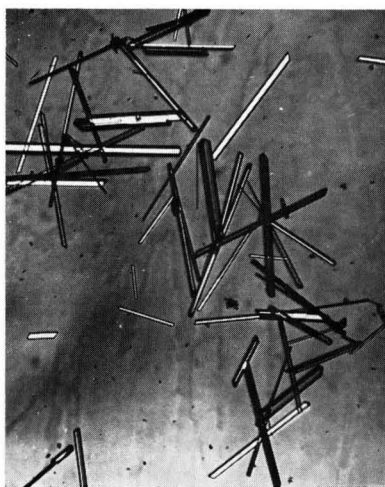


Figure 4. Hemihydrate crystals from a Thiele tube run (80X magnification)

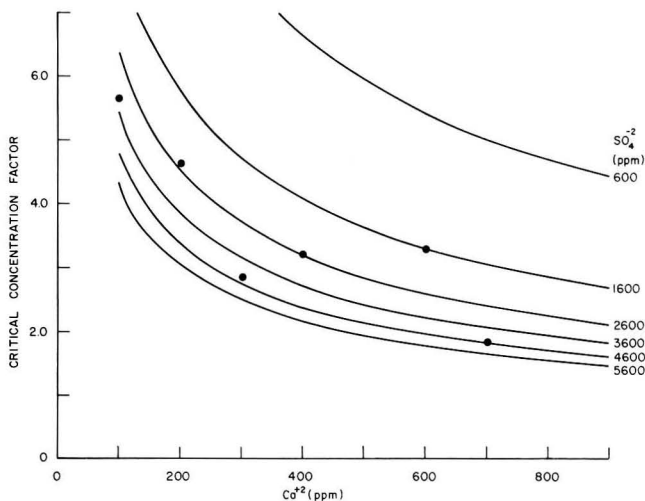


Figure 5. Theoretical critical concentration factor for hemihydrate in sea water at 100°C. vs. calcium and sulfate ion concentrations

- $V_i$  = initial volume in Thiele tube
- $V_b$  = volume added from buret
- $CF_p$  = concentration factor of pre-concentrated water
- $V_f$  = final volume in Thiele tube

**Results and Discussion**

Figure 4 is a photomicrograph of crystals obtained from a typical run on sea water. The needles are hexagonal prisms characteristic of hemihydrate. A sample of this material was purified, dried, and analyzed by x-ray diffraction at the UCLA Department of Geophysics. The crystals were positively identified as pure calcium sulfate hemihydrate.

Data collected thus far on three natural saline waters are presented with analytical data in Table II. The average value obtained for Marineland sea water is approximately 0.1 CF unit higher than the 3.1 figure obtained by Langelier. There

are two possible explanations for this discrepancy. Composition of the two water samples may vary slightly or there may be a small time lag between saturation point (point at which crystals deposit on Carborundum chips) and the point when crystals are first observed suspended in the brine. This lag would cause more water to evaporate, resulting in a slightly larger calculated concentration factor. It would be desirable to determine the true equilibrium solubility of hemihydrate in each water sample and compare this figure with Thiele tube values.

An interesting conclusion may be derived from data presented in Table II. The critical concentration factor for Roswell water is 2.6 compared with 3.2 for Marineland sea water. These data would predict a potentially more serious calcium sulfate scaling problem at the Roswell, N. M., vapor compression distilling plant than a similar plant operating with sea

water. Applying the solubility product principle without regard to salt effect or activity coefficients, we can calculate an ion product (IP) for calcium sulfate in each of the above-mentioned waters.

$$\begin{aligned} \text{Marineland sea water IP} &= [\text{Ca}^{+2}] [\text{SO}_4^{-2}] \\ &= (0.0100) (0.0271) = 2.71 \times 10^{-4} \\ \text{Roswell water IP} &= [\text{Ca}^{+2}] [\text{SO}_4^{-2}] \\ &= (0.0122) (0.0158) = 1.93 \times 10^{-4} \end{aligned}$$

These values are of the same order of magnitude and show that both waters would be supersaturated with respect to calcium sulfate ( $K_{sp} = 2.4 \times 10^{-5}$ ) if other dissolved ions were not present. From these calculations one would also expect approximately the same critical CF value for both waters. In fact, on the basis of these calculations, sea water should deposit calcium sulfate at a lower concentration factor than Roswell water. Since neither of these conditions is met, it is evident that calcium sulfate solubility is strongly influenced by ionic strength of the solution in which it is dissolved. Sea water with a salinity of 35 presents a less serious scaling problem than Roswell water with a salinity of only 16, even though the calcium sulfate ion product is larger for sea water.

The profound effect of background ions on calcium sulfate solubility is clearly demonstrated by this situation. We are concerned not only with total salinity but also with relative distribution and valence type of individual ions. Sea water, for example, has a magnesium ion concentration about four times that of Roswell water. Magnesium and certain other divalent cations have a large positive effect on solubility of sparingly soluble salts. Estimation of solubility from analytical data alone would appear to be a monumental task. The authors believe that scaling potential of any water sample can be most readily determined from good equilibrium solubility measurements or by the method presented in this paper.

One further application of the Thiele tube technique might be considered now. Assume that a certain type of water is treated by ion exchange (McIlhenny, 1965) to remove either  $\text{Ca}^{+2}$  or  $\text{SO}_4^{-2}$  but not appreciably alter the distribution of background ions. Under these circumstances, one would anticipate a higher critical concentration factor. Using Marineland sea water, for example, we know that saturation occurs at 100° C. when  $[\text{Ca}^{+2}]$  and  $[\text{SO}_4^{-2}]$  are about 3.2 times their natural concentration. The following equation may therefore be written for a corrected solubility product constant  $K_{sp}^*$  of hemihydrate in sea water:

$$3.2[\text{Ca}^{+2}] \times 3.2 [\text{SO}_4^{-2}] = K_{sp}^*$$

From Marineland water analysis, converting parts per million to molarity, we may write

$$K_{sp}^* = (3.2)^2 (0.010) (0.027) = 2.75 \times 10^{-3}$$

We can now set up a general equation for the solubility product of calcium sulfate in terms of the critical concentration factor

$$(\text{CF})^2 [\text{Ca}^{+2}] [\text{SO}_4^{-2}] = K_{sp}^* = 2.75 \times 10^{-3}$$

This equation describes the boundary condition for hemihydrate precipitation from sea water at any calcium and sul-

fate concentration. By substituting arbitrary values for  $[\text{Ca}^{+2}]$   $[\text{SO}_4^{-2}]$ , we can solve for CF, using the following relationship:

$$\text{CF} = \sqrt{\frac{2.75 \times 10^{-3}}{[\text{Ca}^{+2}] [\text{SO}_4^{-2}]}}$$

The family of curves shown in Figure 5 was derived by substituting values for calcium and sulfate above and below normal sea water levels. Some experimental verification for the calculated curves has been obtained and data points are shown as circles on the diagram. These data were collected by first stripping Marineland sea water of all calcium and sulfate. Calcium ion was removed by adding a stoichiometric quantity of sodium oxalate, and sulfate ion by adding a stoichiometric quantity of barium chloride. Measured amounts of calcium chloride and sodium sulfate were then added to this depleted water and samples were run by the Thiele tube technique. Figure 5 could be developed for any natural water and would be useful in predicting scaling thresholds if the critical CF value and analytical data on calcium and sulfate content were available and especially would be useful in evaluating the effectiveness of ion exchange softening for prevention of calcium sulfate scale.

#### Acknowledgment

The authors gratefully acknowledge the conscientious efforts of K. Tasugi, K. Fung, and C. Keehn throughout this study. They are also indebted to D. J. Albright for his able glass-blowing services and to E. S. C. Bowler for photomicrography.

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# Adsorption of Viruses on Activated Carbon

## Equilibria and Kinetics of the Attachment of *Escherichia coli* Bacteriophage T<sub>4</sub> on Activated Carbon

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■ Information is needed about the removal of viruses in waste treatment and water purification. Virus removal has been described as adsorption in the activated sludge, flocculation, and filtration processes. Adsorption of *Escherichia coli* bacteriophage T<sub>4</sub> on activated carbon was studied in an agitated solution containing virus and carbon under controlled conditions of temperature, pH, ionic composition, and reactant concentrations. Surface area and particle size distribution were established for the activated carbon. The kinetics of bacteriophage T<sub>4</sub> adsorption on activated carbon can be described by a reversible second-order equation, first-order with respect to both virus and carbon concentration. Adsorption obeys the Langmuir isotherm and is reversible. Virus is not inactivated by adsorption. Adsorption is unimolecular, with very inefficient use of the available carbon surface area, and is of a physical nature and independent of temperature. The virus is probably completely excluded from pores because of its size.

Viruses occurring in water can be introduced into surface waters and municipal sewer systems by human and animal feces (Kelly, 1957). Considerable numbers of enteric viruses are excreted in feces—for example, 10<sup>5</sup> to 10<sup>6</sup> viruses per gram of feces can be recovered from immune humans 6 weeks after administration of Sabin polio vaccine (Sabin, 1955). Typical densities of enteric viruses in sewage average about 7000 viruses per liter of raw, untreated sewage (Clarke and Kabler, 1964).

Contaminated water was implicated in an infectious hepatitis epidemic in New Delhi, India (Dennis, 1959) and in the United States, and polymyelitis virus has been isolated from well and river water (McLean, 1964; Clarke and Chang, 1959). Enteroviruses have caused major problems in swimming pools and along beaches in the United States (Kelly and Sanderson, 1961). Improved methods of handling water for domestic use are obviously needed.

Poppe and Busch (1930) and Pyl (1931) used carbon to adsorb the virus of foot and mouth disease, rendering dilutions of virus noninfectious. Later, after inoculation, carbon released the virus causing infection in guinea pigs. Activated carbon was recently used to adsorb polio virus and infectious hepatitis virus (Clarke and Chang, 1959).

### Materials

West Virginia Pulp and Paper Co.'s Nuchar C-190 activated carbon, derived from a black ash by-product of a chemical pulping process, was used in granular (30-mesh) and powdered form.

Coconut charcoal (4- to 16-mesh) was also evaluated; it was not activated and consequently was not as porous as the activated carbons.

Sieving yielded more uniform particles, deionized water rinses removed dust, and the adsorbents were then dried in thin layers at 105°C. for 24 hours. Stock solutions of known carbon concentration were prepared and sterilized. Adsorbent evaluation was based on the capacity for adsorbing virus, ease of handling, and resistance to further fractionation.

Size 26/35 was obtained from Nuchar C-190 granular carbon (particles passed a U.S. standard sieve No. 26 but were retained on No. 35) and size 120/140 from Nuchar C-190 powdered carbon. Coconut charcoal was rejected because of low capacity. Fracturing was visually noticeable in the granular carbon after 10 hours' agitation, exposing new surface areas and complicating interpretation of the adsorption process. The powdered carbon (Nuchar C-190, size 120/140) was selected for the extensive adsorption studies because it had the highest adsorption capacity for bacteriophage T<sub>4</sub>.

More complete particle-size distributions were determined on the size 120/140 activated carbon, suspended in water to give uniform dispersions for counting, by microscopic observation, with a Porton's Graticule. The 923 carbon particles measured yielded a geometric mean diameter of 2.5 microns and a standard deviation of 2.00. Average surface area was computed by assuming spherical particles, considered justifiable for this carbon: 98.5 × 10<sup>7</sup> sq. microns per mg. of carbon, or approximately 1 sq. meter per gram. Particle concentration in the stock solution was determined microscopically with a counting cell.

The specific surface area of Nuchar C-190 was 700 to 900 sq. meters per gram, based on nitrogen adsorption and application of the Brunauer-Emmett-Teller isotherm (West Virginia Pulp and Paper Co., 1964). Total pore volume was 0.9 cc per gram. The pore-size distribution for Nuchar C-190 was not shown but was assumed to resemble like carbons with average pore diameters of 20 Å. and pore volumes of 0.6 cc. per gram for pore diameters less than 300 Å. Pores with diameters greater than 1200 Å. contribute very little to total pore volume.

The main criteria in selecting a virus were feasibility of assay and stability under adverse conditions. Assay techniques were more advanced for bacteriophages than for animal viruses. Properties of *Escherichia coli* bacteriophages are well established and the host is easily maintained. *E. coli* bacteriophage T<sub>4</sub> (Figure 1) was selected for the present study because of its stability to agitation and temperature changes (Table I).

### Methods

The assay procedure for T<sub>4</sub> bacteriophage was obtained from Robert S. Edgar. Before assaying, the virus solution was diluted in tryptone broth to yield about 300 plaques per plate (Table II). A liquid tryptone top agar mixture was pre-

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Figure 1. Electron micrograph of *Escherichia coli* bacteriophage T<sub>4</sub>

Approximate magnification  $3.4 \times 10^6$ . Negative stain. Provided by Robert S. Edgar, California Institute of Technology

Table I. Properties of *Escherichia coli* Bacteriophage T<sub>4</sub>

Size, m $\mu$	
Head	65 $\times$ 80
Tail	100 $\times$ 20
Diffusion constant at 20° C., sq. cm./sec.	$0.8 \times 10^{-7}$
Specific weight, gram/particle	$3.3 \times 10^{-16}$

pared from 2 ml. of tryptone top agar, 0.15 ml. of a concentrated solution of *E. coli* B cells in the log growth phase, and 0.05 ml. of the virus solution to be assayed. Solidified agar plates were made using a tryptone bottom agar. Tryptone top agar at 45°C. containing the virus and host cells was poured over the bottom agar. After solidification of the top agar, the plates were incubated at 37°C. for 10 hours. Infection of bacterial cells by the progeny of a single virus caused readily distinguishable clear spots, or plaques, which were counted to determine the initial number of viruses.

Duplicate plates from each sample increased the accuracy. Accuracy and reproducibility varied significantly with the growth phase of the host cells. Host cells in the log growth phase yielded three times as many plaques as cells in the endogenous growth phase.

Reproducibility of the assay also varied with incubation time of the plates. The maximum number of plaques was found between 10 and 14 hours of incubation. For shorter periods plaque formation was not complete and for longer periods some plaques were destroyed by antagonistic properties of the host cell.

Table II. Composition of Media for *Escherichia coli* Bacteriophage T<sub>4</sub>

(Constituents per liter of water)

Dehydrated Tryptone	Agar	NaCl
	Tryptone Bottom Agar	
10.0	10.0	5.0
	Tryptone Top Agar	
10.0	6.5	5.0
	Tryptone Broth	
10.0		5.0

Stock solutions of T<sub>4</sub> bacteriophage were prepared by mixing virus with *E. coli* cells in a tryptone agar solution, pouring the mixture on a previously prepared agar plate, and allowing it to solidify. After incubation for 24 hours at 37°C., the bacteriophage was harvested by pouring 5 ml. of tryptone broth on the plate. After about 2 hours, all available virus diffused into the broth, and the liquid was poured off and centrifuged to remove bacterial cells. Virus stock prepared in this manner usually titered  $10^8$  to  $10^9$  virus particles per ml.

*Escherichia coli*, strain B, served as host for T<sub>4</sub> bacteriophage. Log growth phase cells were prepared by inoculating tryptone broth with *E. coli* from the stock culture, followed by incubation for 2.5 hours at 37°C. in a Gyrotory shaker. *E. coli* cells were then collected by centrifuging at 3000 r.p.m. for 20 minutes, and resuspended in fresh tryptone broth.

Glassware was washed in a detergent-alkali mixture to remove positive charges, followed by successive rinses in tap water, distilled water, and deionized water. Sterilization was accomplished in a hot air oven at 200°C. for 1 hour or longer.

During experiments adsorbent and virus were continuously mixed by a Gyrotory incubator shaker at constant temperature. Reaction solutions of known composition were made by adding stock solutions to deionized water in 125-ml. flasks. All stock chemical solutions and deionized water were autoclaved and stored at 4°C. The stock carbon suspension was shaken before use. Solutions were buffered with potassium phosphate to give a pH of 6.9 and ionic strengths of 0.08 and 0.10.

The adsorbent was either allowed to settle or centrifuged at 3000 r.p.m. for 3 minutes before sampling. Centrifugation period caused the virus to descend 0.03 cm. (Cookson, 1966). Samples of 0.1 ml. were withdrawn below 0.5 cm. of the surface and immediately diluted in 9.9 ml. of tryptone broth. Control reaction solutions without adsorbent were run in duplicate at identical temperatures, virus concentrations, and chemical compositions.

#### Preliminary Experimentation

Controls at pH 6.9, ionic strength of 0.10, shaken at 23°C. indicated little loss of virus from natural inactivation (Figure 2). The rate of inactivation in the control was first-order and amounted to 0.004 per hour.

Natural inactivation of virus was not significant in test solutions of pH 7.0 and ionic strengths of 0.02 to 0.20, but was significant at ionic strengths of 0.004. Influence of ionic strength on virus stability has been reported (Sproul, 1957). This phenomenon results from a physical change in the virus

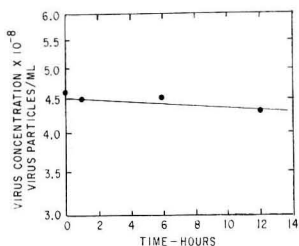


Figure 2. Natural inactivation of virus at pH 6.9 and ionic strength of 0.10

$$C_t = 4.5 \times 10^8 e^{-0.0044t}$$

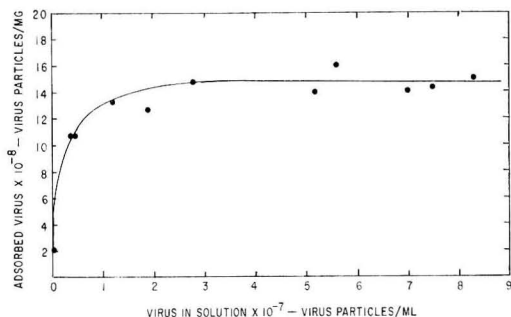


Figure 3. Relation between adsorbed virus per unit weight of carbon and virus concentration in solution at equilibrium

and will be discussed in a later communication on the role of ions in virus adsorption to activated carbon.

The temperature effect on adsorption was examined at 23° and 33°C. No significant difference was noted between the adsorption rates at these temperatures (Cookson, 1966). Physical adsorption processes are weakly dependent on temperature.

Effects of pH and ions on adsorption of bacteriophage T<sub>4</sub> to activated carbon were determined to clarify the mechanism of virus attachment to activated carbon, the role of ions in the primary reaction, and the physicochemical groups involved in the attachment. Detailed results will be presented elsewhere, but optimal adsorption occurred at pH 7.0 and ionic strength 0.08 (Cookson, 1966).

#### Adsorption Equilibrium

Equilibrium was established in the reaction solutions by both a desorption and an adsorption approach using the same carbon. After obtaining adsorption equilibrium, the carbon was removed by centrifugation. The supernatant was carefully removed with a calibrated hypodermic syringe and virus titer assayed. The volume of liquid remaining with the carbon and its titer thus were known. The carbon was then resuspended in a fresh reaction solution identical with that used for adsorption, but with no added virus.

The test solutions were placed on the Gyrotory shaker and assayed after equilibrium was established. The amount of

virus carried over in solution when resuspending the carbon was computed and subtracted from the assay value at equilibrium, giving the net viruses desorbed from the carbon.

Tests were conducted with various initial concentrations of reactants at pH 7.0 and ionic strength 0.08 to determine virus adsorbed per unit of carbon and the virus concentration in solution at equilibrium. The time required to reach equilibrium was determined by periodically assaying adsorption tests over a 28.5-hour period. The amount of additional virus adsorbed after 12 hours (0.37%) was small compared to that adsorbed up to the 12-hour period. Tests run as long as 24 hours usually developed contamination. Equilibrium values, therefore, were presumed to exist after 12 hours of adsorption.

#### Equilibrium Results and Discussion

The adsorption isotherm for bacteriophage T<sub>4</sub> to activated carbon resembles a Langmuir curve (Figure 3). The Langmuir equation can be expressed by

$$c_e/q = \frac{1}{KZ} + \frac{1}{Z}c_e$$

where

$c_e$  = virus concentration in solution at equilibrium, virus particles/ml.

$q$  = virus adsorbed per unit weight of adsorbent at equilibrium, virus particles/mg.

$Z$  = number of sites per unit weight of adsorbent, sites/mg. A site is defined as that which holds one virus particle

$K$  = ratio of forward rate constant to reverse rate constant ( $K = k_1/k_2$ ), ml./virus particle

From a least squares plot values of  $1.6 \times 10^9$  sites per mg. and  $4 \times 10^{-7}$  ml. per virus particle, respectively, were obtained (Figure 4).

Tail fibers were the attaching unit during adsorption on host cells (Puck and Tolmach, 1954; Stent, 1963; Williams and Fraser, 1956). Tail fibers can also cause clumping of bacterial cells, undoubtedly have more than one site for attaching (Wildy and Anderson, 1964), and might also be the attaching units to activated carbon. As with long-chain polymers, a site might accommodate only segments of the chain or fiber. Such an adsorption system might be expected to deviate from the Langmuir isotherm.

Studies suggest that tail fibers are the attaching unit to activated carbon (Cookson, 1966). Tail fibers are not as flexible as long-chain polymers. Although the fibers can bend back and attach to the tail sheath of the virus, they have a fixed configuration when extended. Electron micrographs of extended fibers consistently reveal them as two straight segments with a bend about 900 Å. from the end (see Figure 1). During adsorption different fibers probably occupy about the same number of attaching groups on the carbon. No significant deviation from the Langmuir isotherm would therefore be expected.

Multimolecular adsorption is not suggested by the equilibrium studies, because of agreement of the data with the Langmuir isotherm. Unilayer adsorption of T<sub>4</sub> phage to activated carbon is supported by comparing capacity of the carbon with the area occupied by one virus particle. Such a comparison can be made, since viruses do not agglomerate under the existing testing conditions. Equilibrium studies indi-

cate that carbon capacity was about  $1.6 \times 10^9$  virus particles per mg. of carbon. A surface of 10 sq. cm per mg. was obtained for the 120/140 activated carbon. Dividing surface area by the carbon capacity yields  $5.7 \times 10^{-9}$  sq. cm. for the area of a virus site. The smallest and largest areas that one virus particle could occupy are  $3.3 \times 10^{-11}$  and  $9.6 \times 10^{-10}$  sq. cm. It appears that at maximum only 18% of the available carbon surface was utilized, supporting the model of unimolecular adsorption as predicted by the Langmuir isotherm.

If equilibrium was achieved in the above adsorption tests, it would also be obtained by desorption. T<sub>4</sub> phage was desorbed from carbon used in the previous tests and equilibrium values were determined. The data again corresponded to the Langmuir isotherm (Figure 5). A greater scattering of points, obtained for the isotherm plot, probably resulted from unavoidable experimental errors. Estimation of the amount of unadsorbed virus carried over with the carbon on resuspension reduces the accuracy. The 5-minute period of centrifugation used for removing carbon prior to resuspension later was found to have a small influence on the virus titer.

The method of least squares was used to fit a curve to the desorption equilibrium data (Figure 5). A value of  $1.3 \times 10^9$  sites per mg. of carbon was obtained from the slope, compared to  $1.6 \times 10^9$  when equilibrium was approached by adsorption for the same carbon. The closeness of these values indicates that essentially the same equilibrium was achieved by either adsorption or desorption.

The ability of virus particles to be desorbed from sites on activated carbon is very significant. A chemical reaction does not take place nor is the virus inactivated by adsorption. Electrostatic forces very similar to those involved in adsorption on host cells are responsible for adsorption on carbon (Cookson, 1966). Some investigators have speculated that the injection of viral DNA into host cells resulted from the electrostatic adsorption forces. Viral DNA was not ejected from the protein coat in present studies, however, because this would have created an irreversible process. Reversible adsorption was clearly demonstrated.

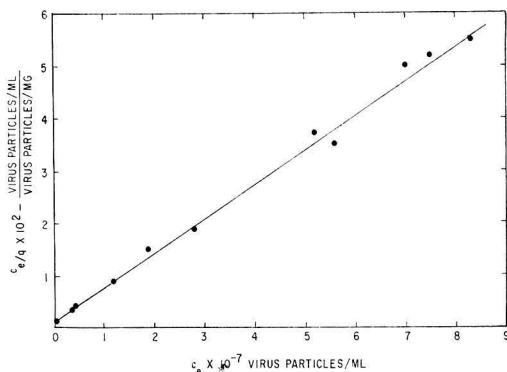


Figure 4. Langmuir plot for adsorption of T<sub>4</sub> phage on activated carbon by least squares analysis

$$c_e/q = 1/KZ + c_e/Z$$

#### Equilibrium in Binary Solutions

In preliminary adsorption tests, tryptone broth caused a greater elution of viruses from carbon than pure buffer solutions of the same pH and ionic strength, suggesting that competition existed between tryptone and virus particles for sites. Viruses were adsorbed on carbon as above and then desorbed with tryptone added to the desorption solution at optimum pH and ionic strength. During adsorption 0.1-ml. samples of carbon plus reaction solution were withdrawn after 30, 60, 180, and 420 minutes and diluted in tryptone broth. Dilutions were 1 to 10, 1 to 100, 1 to 500, and 1 to 1000, yielding many different equilibrium points. Desorption solutions were assayed at various intervals over a 24-hour period to substantiate that equilibrium had been achieved. Total adsorbed and desorbed virus concentrations of each desorption series were known from the dilution factor, so that the amount of virus adsorbed per milligram of carbon could be computed at equilibrium after measuring virus concentration in solution.

Although the Langmuir equation is no longer valid, a qualitative approach can be taken to illustrate that competitive adsorption existed. From a Langmuir plot a value of  $4.2 \times 10^8$  was obtained for the number of sites per milligram of carbon (Figure 6) reduced by tryptone from  $16 \times 10^8$ , explaining the greater elution ability of tryptone buffer compared to plain buffer solutions. The adsorption rate for viruses is probably also reduced.

#### Kinetics

In kinetic experiments various carbon and virus concentrations were buffered at pH 6.9 with potassium phosphate and at ionic strengths of 0.08 and 0.10 (Table III). Test solutions were continuously shaken at 23°C. and sampled periodically.

Adsorption of virus to carbon did not follow a first-order reaction. The expected relationship between adsorption rate and reactant concentrations would be first-order with each reactant and, therefore, second-order overall.

Equilibrium studies showed that adsorption is reversible. During the initial stages, however, the rate of the reverse re-

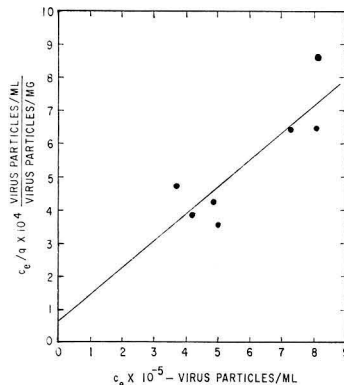


Figure 5. Langmuir plot for desorption of T<sub>4</sub> phage from activated carbon by least squares analysis

$$c_e/q = 1/ZK + c_e/Z$$

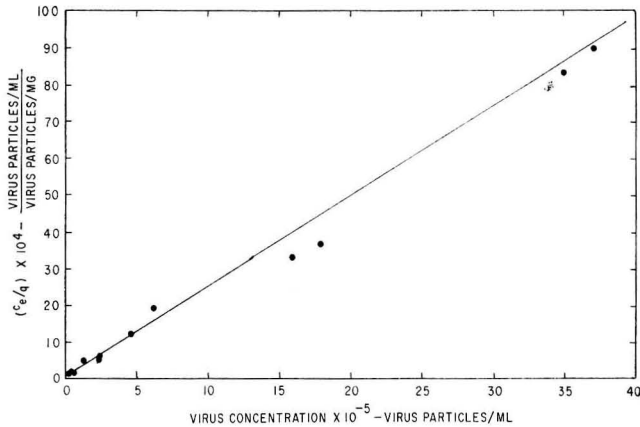


Figure 6. Langmuir plot for desorption equilibrium in tryptone broth by least squares analysis

$$c_d q = 1/KZ + c_d Z$$

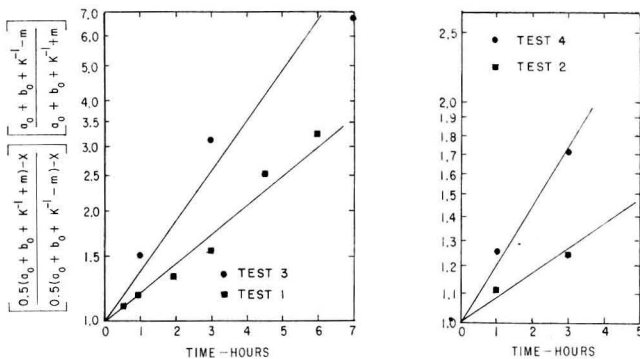
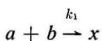


Figure 7. Reversible second-order kinetic plot of tests 1 to 4 for adsorption of T<sub>4</sub> phage on carbon

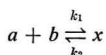
action is negligible and the data can be interpreted by irreversible kinetics. The mathematical representations of an irreversible and reversible system are given below.

IRREVERSIBLE



$$\ln a/b = (a_0 - b_0)k_1 t + \ln a_0/b_0 \quad (1)$$

REVERSIBLE



$$tk_1 m = \ln \left[ \frac{0.5(a_0 + b_0 + K^{-1} + m) - x}{0.5(a_0 + b_0 + K^{-1} - m) - x} \right] \times \left[ \frac{a_0 + b_0 + K^{-1} - m}{a_0 + b_0 + K^{-1} + m} \right] \quad (2)$$

where

$a_0$  = initial concentration of virus, viruses/ml.

$b_0$  = initial concentration of carbon sites, sites/ml.

$a$  = virus concentration at time  $t$ , viruses/ml.

$b$  = site concentration at time  $t$ , sites/ml.

$t$  = time, sec.

$k_1$  = forward rate constant, ml./virus-sec.

$k_2$  = reverse rate constant, 1/sec.

$K$  = equilibrium constant ( $K = k_1/k_2$ ), ml./virus.

$x$  = concentration of adsorbed virus at time  $t$ , virus/ml.

$m = [(a_0 - b_0)^2 + K^{-1}(2a_0 + 2b_0 + K^{-1})]^{1/2}$

Interpreting two adsorption tests by the irreversible equation provides a procedure for calculating the two unknowns of the system: initial concentration of carbon sites and forward rate constant. The rate constant is independent of site and virus concentrations, and the site concentrations of two



Table III. T<sub>4</sub> Phage Adsorption on Carbon Using Different Initial Concentrations of Reactants

Time, Hr.	Test No.							
	1	2	3	4	5	6	7	8
	Carbon, Mg./Liter							
	250	50	100	25	250	250	250	Zero
	Virus Particles per Ml. Remaining in Solution							
0	4.8 × 10 <sup>8</sup>	1.0 × 10 <sup>8</sup>	1.0 × 10 <sup>8</sup>	1.05 × 10 <sup>8</sup>	1.2 × 10 <sup>8</sup>	1.5 × 10 <sup>7</sup>	4.7 × 10 <sup>8</sup>	4.6 × 10 <sup>8</sup>
0.5	...	...	...	...	3.8 × 10 <sup>7</sup>	5.4 × 10 <sup>6</sup>	2.7 × 10 <sup>8</sup>	4.3 × 10 <sup>8</sup>
0.6	2.4 × 10 <sup>8</sup>	...	...	...	...	...	...	...
1.0	2.2 × 10 <sup>8</sup>	7.0 × 10 <sup>7</sup>	4.7 × 10 <sup>7</sup>	9.1 × 10 <sup>7</sup>	2.4 × 10 <sup>7</sup>	3.6 × 10 <sup>6</sup>	2.2 × 10 <sup>8</sup>	4.5 × 10 <sup>8</sup>
1.8	1.5 × 10 <sup>8</sup>	...	...	...	...	...	...	...
2.0	...	...	...	...	1.6 × 10 <sup>7</sup>	1.3 × 10 <sup>6</sup>	...	...
3.0	1.1 × 10 <sup>8</sup>	5.7 × 10 <sup>7</sup>	1.7 × 10 <sup>7</sup>	8.0 × 10 <sup>7</sup>	7.6 × 10 <sup>6</sup>	4.6 × 10 <sup>5</sup>	8.6 × 10 <sup>7</sup>	...
4.0	...	...	...	...	9.0 × 10 <sup>6</sup>	2.9 × 10 <sup>5</sup>	...	...
4.5	6.3 × 10 <sup>7</sup>	...	...	...	...	...	7.9 × 10 <sup>7</sup>	...
5.5	...	...	...	...	6.7 × 10 <sup>6</sup>	2.0 × 10 <sup>5</sup>	...	...
6.0	4.3 × 10 <sup>7</sup>	...	...	...	...	...	5.5 × 10 <sup>7</sup>	4.5 × 10 <sup>8</sup>
7.0	...	5.8 × 10 <sup>7</sup>	6.0 × 10 <sup>6</sup>	9.2 × 10 <sup>7</sup>	3.2 × 10 <sup>6</sup>	8.0 × 10 <sup>4</sup>	...	...
12.0	...	...	...	...	...	...	...	4.3 × 10 <sup>8</sup>
13.5	...	5.1 × 10 <sup>7</sup>	4.1 × 10 <sup>6</sup>	7.9 × 10 <sup>7</sup>	...	...	...	...
23.5	...	...	3.9 × 10 <sup>6</sup>	7.3 × 10 <sup>7</sup>	...	...	...	...

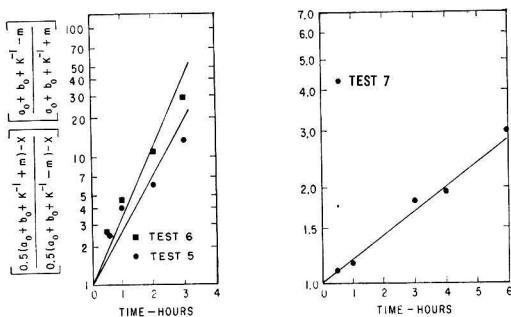


Figure 8. Reversible second-order kinetic plot of tests 5, 6, and 7 for adsorption of T<sub>4</sub> phage on carbon

tests vary in proportion to their carbon concentrations. This procedure gave an average value of 1.9 × 10<sup>9</sup> sites per mg. of carbon and a forward rate constant of 6.5 × 10<sup>-13</sup> per second, compared with 1.6 × 10<sup>9</sup> sites per mg. of carbon obtained from equilibrium studies.

A better representation would be reversible second-order kinetics. The adsorption data presented in Table III were linearized by plots of

$$\ln \left[ \frac{0.5(a_0 + b_0 + K^{-1} + m) - x}{0.5(a_0 + b_0 + K^{-1} - m) - x} \right] \left[ \frac{a_0 + b_0 + K^{-1} - m}{a_0 + b_0 + K^{-1} + m} \right]$$

vs. *t* (Figures 7 and 8). Values of 4.0 × 10<sup>-7</sup> ml. per virus particle and 1.9 × 10<sup>9</sup> sites per milligram were used for the equilibrium constant, *K*, and the number of sites per milligram of carbon, *b*<sub>0</sub>, respectively.

The forward rate constant, *k*<sub>1</sub>, was obtained from the slopes of each plot (Figures 7 and 8 and Table IV). The reverse rate constant, *k*<sub>2</sub>, was then calculated from the equilibrium constant. These rate constants should be identical for all tests

Table IV. Rate Constants for Adsorption of Bacteriophage T<sub>4</sub> on Activated Carbon at pH 6.9 and Ionic Strengths of 0.08 and 0.10

Test No.	Ionic Strength	Figure	Rate Constants	
			Forward <i>k</i> <sub>1</sub> × 10 <sup>13</sup>	Reverse <i>k</i> <sub>2</sub> × 10 <sup>7</sup> sec. <sup>-1</sup>
1	0.10	7	0.161	7.2
2	0.08	8	0.091	8.3
3	0.08	7	0.304	8.8
4	0.08	8	0.192	8.3
5	0.08	9	1.022	8.1
6	0.10	9	0.131	7.9
7	0.08	10	0.188	8.6

of like pH, ionic strength, and temperature, given the proper values of *K* and *b*<sub>0</sub> used in Equation 2.

The rate constants varied little. At ionic strengths of 0.08 and 0.10, the forward rate constants ranged from 8.3 × 10<sup>-13</sup> to 8.8 × 10<sup>-13</sup> and 7.2 × 10<sup>-13</sup> to 7.9 × 10<sup>-13</sup> ml. per virus particle-second, respectively. This variance for a particular ionic strength is reasonable and indicates that reversible second-order kinetics can be used to represent the adsorption process.

Conclusions

The same equilibrium was obtained by either adsorption or desorption. The reversible nature of the adsorption process was also demonstrated by greater desorption in the presence of a competitive adsorbate, tryptone. Adsorption and desorption did not alter the infecting ability of the virus.

Adsorption of bacteriophage T<sub>4</sub> on activated carbon can be represented by the Langmuir isotherm. Such agreement suggests formation of a unimolecular layer. The maximum surface coverage of the adsorbent was estimated at only

18%. This small surface coverage not only confirms single layer adsorption, but also indicates that pore areas are probably not utilized. The size of phage T<sub>4</sub> probably completely excludes it from pores. All carbon sites must be approximately equal in their adsorbing ability. Application of the Langmuir isotherm yielded a carbon capacity of  $1.6 \times 10^9$  sites per mg.

*Escherichia coli* bacteriophage T<sub>4</sub> adsorption on activated carbon can be described by reversible second-order kinetics. Adsorption was first-order with respect to both virus concentration and carbon sites. Equilibrium constant and carbon capacity as determined by the Langmuir isotherm gave satisfactory linearization of data when used in the reversible second order equation.

#### Acknowledgment

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## Biophysical Limnology

### Separation of Suspended and Colloidal Particles from Natural Water

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■ Many materials in the size range of suspended particles (10  $\mu$  to 200 microns) contribute to water pollution. Such particles are heterogeneous with wide ranges of size, shape, density, and metabolic or surface activity. The distribution of many species is discontinuous and the concentration in a given volume of water is often too low for direct study. This laboratory has been developing biophysical methods, principally centrifugal, for investigating suspended particles in water. Continuous-flow, density-gradient, and zonal centrifugation are yielding most promising results for concentrating, isolating, and purifying suspended particles from large volumes of water. Centrifugal processes can yield information about density, size, and sedimentation rate. Monitoring the effluent stream from the centrifuge can yield information on chemical composition, concentration, and biological activity. Bioassay, x-ray diffraction, and electron microscopy can be used with the particles from the effluent. This laboratory is systematically investigating the physical and chemical characteristics of particles suspended in water. These data are useful in designing density gradients, centrifugal processes, and equipment, and helping to pinpoint the location of particular species of particles, such as viruses, in the effluent after centrifugation. Since large volumes of water may be used as the initial sample (up to 100 liters), the sensitivity of detection is significantly greater than by other methods.

Qualitative and quantitative fractionation of the various organic and inorganic species of particles occurring in natural water is a prerequisite to investigations of cycling of biologically or surface active contaminants in the aquatic biosphere. With the increasing release of these contaminants coinciding with increasing re-use of water, interest is developing in means of assessing the possible biohazard the contaminants may present. Evidence from this laboratory shows that contaminants such as radionuclides are not found in a single fraction, but are differentially distributed among the various fractions of the water mass (Lammers, 1964). The fraction with which the contaminant is associated determines to a large degree its importance as a biohazard, since it also determines how much of the contaminant enters the food chain and to some extent the degree of bioconcentration one can expect.

This paper deals chiefly with the suspended and colloidal-sized organic particles typically found in natural water, although the same theories and general methods apply to similar particles in other fluids and to inorganic particles. Generally, centrifugal methods are not practical for particles with a molecular weight of less than  $10^6$  and a sedimentation

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rate of less than 10 *S* (Svedberg constant) when dealing with large volumes of fluid.

The investigation of particulate fractions in natural water is complicated by their heterogeneity, irregular distribution, and the low population levels of some important types. The scarcity and irregular distribution of some species of particles in a given volume of water can be circumvented by using large-volume samples and proportional-flow or other statistically designed method of sampling. This means that there must be some means of rapid separation and concentration of the particles from the suspending water so that the volume is reduced to a manageable size. Meaningful analysis of the concentrated particles is not possible unless the various types of particles in the sample, together with their sorbed contaminants, are separated into relatively homogeneous fractions. The fractionation must be rapid and cause minimum distortion and injury to the particles and minimum loss of sorbed contaminants. The groups of relatively homogeneous particle fractions resulting from the concentration and fractionation should reflect accurately the make-up of the natural water mass, and an analysis should indicate the distribution, as well as the total load, of particles of interest and contaminants within the water mass. From this information the potential biohazard may be accurately assessed.

#### Materials, Methods, and Results

To approach the problem in a logical, systematic way, based upon the experience gained in water fractionation during the past 8 years, what was known of the chemical, biological, and physical characteristics of the suspended, colloidal, and dissolved particles reported in natural water was assessed. The characteristics thought most useful, considering the success of biophysical separations for biological tissues and our own past experience, are banding density, sedimentation rate, particle size and shape, and the expected concentration range. Information on chemical composition, charge or surface activity, and biological activity is also useful. A survey of the literature showed little information on these characteristics for water-borne particles. The characteristics for the suspended organic particles have been determined experimentally in this laboratory. The data on colloidal organic particles (virus and virus-like), gathered from other sources (Burnet and Stanley, 1959; Lammers, 1966b) and to some extent verified in this laboratory, show that the density range for suspended organic particles (0.5 to 40 microns) is from a minimum of 1.1 to a maximum of 1.23 grams per cc. These data are for the density of the particles at their isopycnic point in the gradient material 3,5-DP [the methylglucamine salt of 3,5-diiodo-4-pyridone-*N*-acetic acid (Lammers, 1966a)]. The density of the colloidal organic particles ranges from a minimum of 1.295 to a maximum of 1.65 grams per cc. These data are for the density of the particles at their isopycnic point in the gradient material CsCl.

If one makes a semilog plot with sedimentation rate (log) as the ordinate and buoyant density as the abscissa (Figure 1), it becomes apparent that few if any particles of the representative organic and inorganic types plotted share both the same density and the same sedimentation rate. The particles fall into seven major categories, rather well separated from each other: (1) algae; (2) bacteria; (3) organic colloids, including viruses; (4) organic macromolecules; (5) suspended inorganic particles; (6) colloidal inorganic particles; and (7) dissolved inorganic

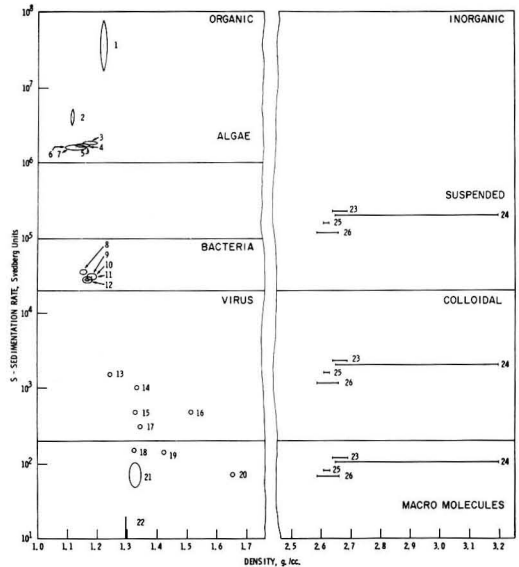


Figure 1. Banding density and sedimentation rates of selected particles typical of water

Data show grouping of related particles and regions devoid of particles separating groups into well defined fractions. Densities for 1 to 12, banding densities in 3,5-DP. Densities for 13 to 22, banding densities in CsCl. Densities for 23 to 26, banding densities reported in literature and verified in thallium formate gradients

Key No.	Name
1	<i>Euglena</i> sp.
2	<i>Chlamydomonas</i> sp.
3	<i>Scenedesmus</i> sp.
4	<i>Spongiochloris excentrica</i>
5	<i>Dictyosphaerium puchellum</i>
6	<i>Chlorella vulgaris</i>
7	<i>Saccharomyces cerevisiae</i>
8	<i>Aerobacter aerogenes</i>
9	<i>Serratia marcescens</i>
10	<i>Escherichia coli</i>
11	<i>E. freundii</i>
12	<i>Proteus vulgaris</i>
13	Newcastle virus
14	T <sub>2</sub> phage
15	Adeno-2 virus
16	T <sub>3</sub> phage
17	Shope papilloma virus
18	Polio virus
19	Foot and mouth virus
20	Ribosomes
21	Turnip yellow mosaic virus
22	Bovine serum albumin
23	Illite
24	Vermiculite
25	Kaolinite
26	Quartz

particles. Techniques which will separate the particles on the basis of their sedimentation rate differences should fractionate the heterogeneous particles in a sample into fractions homogeneous for sedimentation rate. If one can also separate the particles on the basis of density differences, the initial sample should be fractionated into the seven rather homogeneous groups plotted in Figure 1. For present purposes, suspended particles are considered to have sedimentation rates between  $2 \times 10^4$  and  $10^7$ , colloids between  $10^2$  and  $10^4$ , and macromolecules and dissolved particles less than 200 *S*.

**Centrifugal Methods.** The course of development of water fractionation by various biophysical techniques has been covered (Lammers, 1964, 1966). Two types of centrifugation have been found most useful in water fractionation: continuous-flow and density-gradient. The first is based in theory upon differences in sedimentation rate of different types of particles and may be used to concentrate and separate the particles from the suspending water and also for partial isolation of the particles into groups homogeneous for sedimentation rate. Density-gradient centrifugation may then be used to fractionate the concentrated particles on the basis of density differences. Combinations of these techniques are used to concentrate the particles from the suspending water and isolate them into groups which are homogeneous for both sedimentation rate and density. For the current experimental period, certain major fractions were designated for isolation into separate fractions. Figure 2 shows the present flow chart for the concentration and isolation of these fractions. Many fractions could be isolated from a large-volume sample, but at present only major groups or groups of special interest are isolated as separate fractions.

**Suspended Particles. CONTINUOUS-FLOW CENTRIFUGATION.** To ensure a sufficient number of particles of any one type, the initial sample must be large enough to contain particles of interest in sufficient numbers for analysis. This initial volume, based on experimentally determined population estimates, may range from 2 to 50 liters. At present continuous-flow centrifugation is the method of choice for concentration of the particles from the water, since it can be done rapidly and at a low temperature (5° C.) to slow chemical and biological changes in labile particles.

By adjusting the speed of the centrifuge rotor and the flow rate of the liquid influent through the rotor, one alters the total centrifugal force upon the particles in the centrifugal field (gravities  $\times$  minutes). The suspended particles can then be separated on the basis of their differences in sedimentation rate. By passing the supernatant through a second or third continuous-flow centrifugation (a cascade), with an increased centrifugal field, the initial water sample can be separated into fractions based on sedimentation rate. The particles sedimented to the periphery of the centrifugal field are allowed to collect on the rotor wall, where they may be removed at the end of the centrifugation. In a triple cascade through a continuous-flow centrifuge, four initial fractions are collected: (1) suspended particles of about 4 microns and larger ( $10^6$  to  $10^7 S$ ); (2) suspended particles smaller than 4 microns ( $2 \times 10^4$

to  $10^6 S$ ); (3) colloids ( $2 \times 10^2$  to  $2 \times 10^4 S$ ); and (4) macromolecules and dissolved particles in the final supernatant (less than  $2 \times 10^2 S$ ).

**DENSITY-GRADIENT CENTRIFUGATION.** After the initial fractionation based on sedimentation rate, the pellet of mixed organic and inorganic particles from the suspended particle fraction is thoroughly resuspended and carefully introduced to the centripetal side of a preformed density gradient of 3,5-DP with a density range from a minimum of 1 to a maximum of 1.5 grams per cc. This is centrifuged to a force sufficient to band  $2 \times 10^4 S$  organic particles (56,000 gravities  $\times$  minutes) at their isopycnic points. The density gradient containing the banded organic particles is pumped through the optical flow cell of a densimeter operating at 530 m $\mu$ , the range of minimum absorption of 3,5-DP, and the number of particles in each band is recorded in terms of absorbance (Figure 3). Since the density and sedimentation rate of the particles are known, the particles can be identified with some certainty by the position of the band in the density gradient. After passing through the flow cell, the isolated fractions are collected in a fraction collector and transferred to a dialysis sac, and the gradient material is dialyzed away against a pH 7.2 buffer. Following dialysis an appropriate bioassay is carried out with the isolated fractions, and they may be examined with optical or electron microscopy for a more exact count and identification.

The inorganic particles from the density-gradient centrifugation, with a density range from 2.6 to 3.2, are too dense to band in 3,5-DP and sediment to the periphery of the centrifugal field where they may be collected as a single pellet. These particles may be handled as a single fraction, or resuspended and fractionated further on the basis of differences in sedimentation rate for particles of different sizes.

**Colloidal Particles.** The colloids may be separated into an organic and an inorganic fraction in the same way as the suspended particles but using a greater total centrifugal force ( $5.4 \times 10^6$  gravities  $\times$  minutes at  $R_{av}$ ). Since these colloidal particles are not very sensitive to changes in osmotic pressure, either CsCl or 3,5-DP may be used as a gradient material. An example of this type of fractionation is a current investigation of populations of virus-like particles in water. In this investigation after the initial continuous-flow centrifugation to a sediment  $2 \times 10^4 S$  particles, the supernatant is recentrifuged to sediment the particles in the virus range ( $2 \times 10^2$  to  $10^4 S$ ). The colloidal pellet, containing any particles of a viral nature, is resuspended and introduced to the centripetal side of a preformed density gradient and centrifuged to density

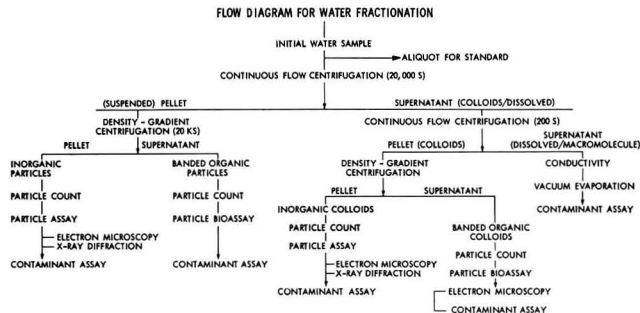


Figure 2. Scheme of fractionation and analysis of a water sample

equilibrium ( $14.4 \times 10^6$  gravities  $\times$  minutes at  $R_{av}$ ). After centrifugation is complete, the gradient is pumped from the rotor through an optical flow cell and peaks of absorption are recorded as absorbance (Figure 4). The isolated particles are recovered, dialyzed free of the gradient, and bioassayed for bacteriophage activity. An aliquot of each isolated fraction is examined by electron microscopy (Figure 5). Bacteriophage particles from water samples with an initial phage concentration of 2 active particles per liter have been detected regularly by plaque assay. Unidentified particles are recorded as density bands and as virus-like particles by electron microscopy, but so far there is no indisputable evidence that these orphan particles are, in fact, viral.

**Macromolecules and Solutes.** At present macromolecules and solutes are recovered as the supernatant of the 200 S continuous-flow centrifugation and concentrated by vacuum evaporation at 35° C. This fraction is not subdivided but is treated as a single entity, since the major effort is now concentrated on centrifugal methods which are unsuitable for these particles. Current analyses for this fraction yield data on the total contaminant load in the macromolecule-dissolved particle fraction.

The fractions isolated by the techniques outlined are characterized by suitable analytical techniques to determine both the size of the fraction (number of particles) and the identity of the particles in the fraction. These techniques include ultraviolet and infrared absorption, electron microscopy, x-ray diffraction, and conductivity. Following this, each of the isolated fractions, plus an unfractionated aliquot of the original sample, is analyzed for the contaminant of interest.

#### Discussion

**Density Gradients.** With current density-gradient preforming pumps, it is possible to take advantage of density differences as small as 0.005 gram per cc. between species of organic particles and to band these species into relatively pure sub-fractions within the total organic fraction. This has been done in individual experiments with mixtures of pure cultures grown in the laboratory (Figure 3). However, some species (Figure 1) in the suspended particle-size range are not uniform and overlap in density and sedimentation rates so that they cannot be cleanly separated by centrifugal techniques.

The density and sedimentation rate differences among virus species are sufficiently great and the particles of a species are

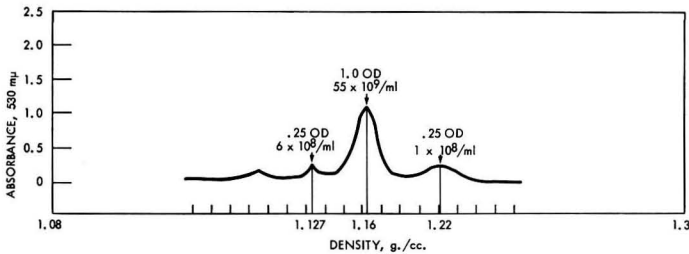


Figure 3. Absorbance recording of separation of three laboratory-cultured species of algae centrifuged to density equilibrium in a 3,5-DP density gradient

*Chlorella vulgaris* banded at a density of 1.127, *Dictyosphaerium puchellum* at 1.16, and *Euglena sp.* at 1.22

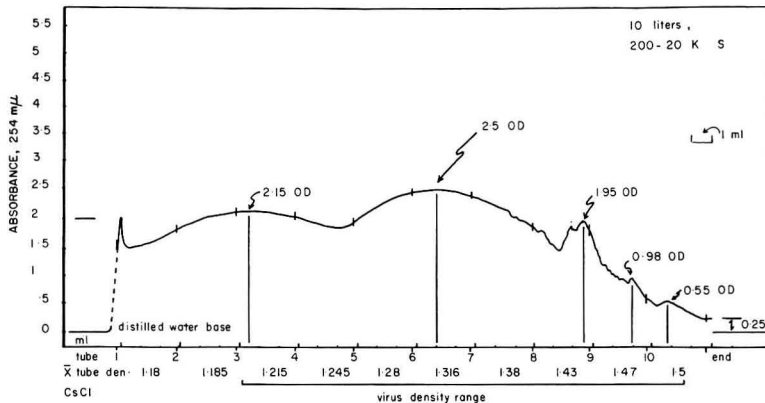


Figure 4. Recording of separation of colloidal organic particles from a sewage-contaminated stream

Particles centrifuged to density equilibrium in a CsCl density gradient after being concentrated from original water sample by differential centrifugation. Plaque assay of three peaks on right indicated presence of coli-phage at this density zone



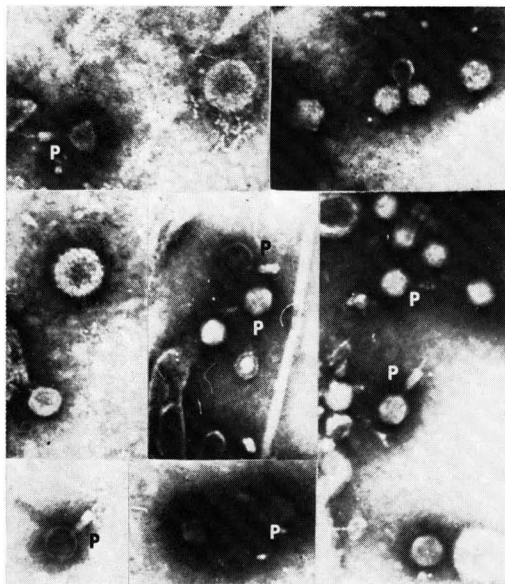


Figure 5. Electron micrograph of selected organic colloids recovered by centrifugal techniques from a water sample from Watts Bar Dam tailrace

Phosphotungstate negative staining (80,000  $\times$  magnification)

sufficiently uniform to make possible separations between most virus species (Figures 1 and 4).

The best results in this laboratory have been obtained with the gradient material 3,5-DP, which is physiologically inert and has a low viscosity and a maximum density of 1.5 (Lammers, 1966a). Many species, such as ciliates and flagellates, survive in an inactive but intact form after density-gradient centrifugation in 3,5-DP, but in sucrose, and still more in CsCl gradients, not even "ghosts" of these delicate forms survive. Microscopic examination shows that osmotic-sensitive particles are less plasmolyzed in 3,5-DP than in either sucrose or CsCl and the particles do not measurably decrease in size.

Osmotic-sensitive particles exhibit a banding (isopycnic) density directly related to the gradient material used. Generally, these particles are the suspended organic particles (from 0.1 to 40 microns) chiefly bacteria, algae, and some fungi. As water osmoses out of the particles, because of the osmotic pressure of the gradient, the particle becomes denser as the ratio of water to nondiffusing cellular constituents changes. In addition, if the gradient molecules enter the particle, the density of the particle is increased further, so it migrates in the centrifugal field into regions of still higher density where the osmotic effect is repeated. The result is a higher recorded density than the particle actually has.

It is possible to minimize the osmotic effects of the density gradient by using a gradient material which is dense in low molar concentrations, is a nonelectrolyte, and has a relatively large, nonosmosing molecule. 3,5-DP is dense in low molar concentrations, but unlike sucrose it is an electrolyte, so its osmotic pressure is slightly higher than that of sucrose. How-

ever, the size of the 3,5-DP molecule inhibits its entry into the osmotic-sensitive particles, minimizing the effects of the density increase.

Suspended organic particles isolated in 3,5-DP density gradients have a lower apparent density than in either sucrose or CsCl gradients and we assume that this lower density, while not the true density of the particle, is closer to that true density than the values from other gradients tested. The lower apparent density of the particles banded in 3,5-DP is probably due to the slow entry of the nonosmosing 3,5-DP molecules into the particle compared with the more rapid entry of sucrose or CsCl. The density increase in 3,5-DP then appears mostly due to loss of water and not to entry of the gradient molecules. Since colloidal particles are less osmotic-sensitive than suspended particles, CsCl is a suitable gradient material for banding and characterizing colloids.

**Sensitivity.** This biophysical concentration and isolation technique allows investigation of particles which exist in extremely small concentrations along with their sorbed contaminants. The method yields good qualitative and quantitative results which may be extrapolated to fit the original water mass. In addition, the ability to handle large-volume samples is increasing, so that even rarer particles may be isolated in numbers within the sensitivity of analytical instruments available now.

Nonliving particles, organic and inorganic, may be isolated and concentrated to a final concentration of  $2 \times 10^6$  physical particles per ml. from 20-liter water samples where the initial particle concentration is  $10^2$  per ml. If those  $10^2$  particles per ml. had sorbed radionuclides with an activity as low as  $10^{-3}$   $\mu\text{c.}$  per ml., the final radionuclide activity level, after concentration, would be 20  $\mu\text{c.}$  in the fraction, which is within the sensitivity limit of a good instrument. Larger samples may be collected if particles of interest occur in concentrations lower than  $10^2$  per ml.

Biologically active particles may be identified even when they exist in numbers less than  $10^2$  per ml. in the original sample. In theory a single biologically active particle is all that is required for a bioassay, and it should be possible to isolate and culture a single cell from a 20-liter initial sample ( $5 \times 10^{-5}$  particle per ml.). At present it is routine to detect coli-phage particles from a 20-liter sample with an initial phage concentration of  $5 \times 10^{-4}$  active particle per ml. However, for the detection of radionuclide accumulation, the same limits of particle numbers and sensitivity apply for biologically active particles as for inorganic particles.

#### Presentation of Results

The final results may be presented in several ways: the kinds and amount of particles found in any fraction, the relative distribution of a contaminant among the various isolated fractions, the actual amount of a contaminant accumulated by the various fractions, and a single fraction, such as virus-like particles (organic colloids), may be singled out for further investigation. If the entire sample is fractionated and each fraction analyzed, the result is a "balance sheet" of the total load of a contaminant and its distribution.

As suggested earlier, the number of fractions of homogeneous particles which may be isolated from the water is limited to a large extent by the time available and the volume of the original sample.

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## Role of Fluid Properties in Gas Transfer

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■ Considerable attention has been directed to the determination of the capacity of a river to assimilate organic pollution. One aspect of this problem is the prediction of river aeration, which depends on an adequate knowledge of the mechanism of absorption of low-solubility gases into a turbulent fluid. Reported herein are the results of an experimental and theoretical study which was undertaken to extend the usefulness of previous work on the film penetration model for gas absorption coefficients. Proposed relationships for surface renewal frequency and the film thickness were verified and then used in the model to predict effects of temperature on oxygen absorption which are in good agreement with values reported in the literature.

The rate of change of concentration of dissolved gas in a liquid of volume,  $V$ , which is assumed to be of uniform concentration,  $C_L$ , is

$$\frac{dC_L}{dt} = \frac{K_L A_s (C_s - C_L)}{V} \quad (1)$$

where  $C_s$  is the saturation concentration,  $A_s$  is the surface area, and  $K_L$  is the absorption coefficient. Solution of Equation 1 for an initial liquid concentration of  $C_0$  yields the familiar logarithmic absorption equation

$$\ln \left( \frac{C_s - C_0}{C_s - C_L} \right) = \frac{K_L A_s t}{V} \quad (2)$$

The actual surface area,  $A_s$ , is difficult to measure in turbulent fluids and the horizontal projection of the actual surface area,  $A_o$ , is often used. For this discussion, they are related by

$$A_s = C_A A_o \quad (3)$$

where  $C_A$  is a coefficient depending on flow conditions and other factors. Absorption coefficients computed by using  $A_o$  are designated by primes in this work. They are related to those calculated by using  $A_s$  by

$$K_L' = C_A K_L \quad (4)$$

where  $K_L'$  is termed the apparent absorption coefficient and  $K_L$  is termed the true absorption coefficient.

When these equations are applied to streams it is common to

refer to the quantity  $(C_s - C_L)$  as  $D$ , the dissolved oxygen deficit. Further, the quantity  $A_o/V$  equals the average depth,  $H$ . Then for streams

$$\frac{dC_L}{dt} = \frac{K_L' A_o D}{V} = \frac{K_L' D}{H} = K_2 D \quad (5)$$

where  $K_2$  is termed the reaeration coefficient, which is equal to the apparent absorption coefficient divided by the depth.

### Models for Gas Absorption

Various theories of gas absorption result in different equations for the determination of the absorption coefficient,  $K_L$ . Lewis and Whitman (1924) assumed that there is a stagnant film at the liquid surface in which steady-state molecular transfer controls the rate of mass transfer. This theory results in a value of  $K_L$  equal to the molecular diffusivity,  $D_m$ , divided by the film thickness,  $L$ . Conversely, the penetration theories of Higbie (1935) and Danckwerts (1951) abandon the film concept and propose that the interface is continuously replaced by eddies which control the rate by unsteady-state molecular transfer. Their models result in values of  $K_L$  proportional to the square root of  $D_m$ .

The divergence of these results concerning  $K_L$  may have been resolved with the suggestion that the film may be assumed to maintain its existence in a statistical sense (Dobbins, 1956). The film is considered to be always present; but its composition is continuously changed by liquid from beneath the surface. Indeed, surface films have been reported (Bolin, 1960; Kanwisher, 1963; Davis and Crandall, 1930), and the proposed stochastic nature of the existence of the film is in accord with ideas of fluid turbulence. The resulting film penetration model for  $K_L$  is

$$K_L = \sqrt{D_m r} \coth \sqrt{\frac{rL^2}{D_m}} \quad (6)$$

where  $r$  is the frequency of replacement of the liquid film. This equation reduces to Danckwerts' equation ( $K_L = \sqrt{D_m r}$ ) as the coth term becomes about 3 or greater and approaches the film equation ( $K_L = D_m/L$ ) as the renewal rate,  $r$ , approaches zero.

The effect of molecular diffusivity on the absorption coefficient has often been measured in attempts to verify various theories of gas absorption. This effect is usually expressed by showing how the value of  $K_L$  varies with  $D_m$  raised to an

exponent,  $n$ . The Lewis and Whitman theory is represented by an exponent of unity, while the theories of Higbie and Danckwerts have values of 0.5. It is significant that Equation 6 has the property that the exponent can vary from 0.5 to unity. Experimental data previously reported (Dobbins, 1964) demonstrated a variation in the exponent for an aeration system with the turbulence generated from below the surface. The higher values of the exponent were obtained for experiments conducted at low mixing intensities. Subsequent experiments in a similar system (Metzger, 1965) showed that  $n$  approaches a constant value at high mixing intensities. This constant appears to be 0.5, in accord with the predictions of Equation 6, although the exact value depends on a precise knowledge of the molecular diffusion coefficients.

Equation 6 was further verified by direct application to stream aeration (Dobbins, 1964). Absorption coefficients reported for a wide range of stream conditions were compared with those computed using Equation 6 along with those computed using the O'Connor-Dobbins equations (1956) and the Churchill-Elmore-Buckingham formula (1962). This latter comparison demonstrated that Equation 6 provided results superior to the other formulas over a broad spectrum of conditions.

The film penetration model may be employed as a workable representation of the gas absorption phenomenon as it is encountered in natural rivers. However, its usefulness is somewhat limited by the lack of a verified theory for the determination of  $r$ , the frequency of replacement of the liquid film, and  $L$ , the film thickness.

#### Proposed Equations for $r$ and $L$

The surface of pure water is not a monomolecular layer with unaltered liquid immediately underneath it, but a zone in which molecules are oriented (Drost-Hansen, 1965). The orientation is in the direction of polarization (Weyl, 1951) and may extend to depths of  $10^{-5}$  cm. (Henniker, 1949). It is to this orientation that the surface tension and elastic strength (Henniker, 1949) of pure water surface are ascribed. Since the surface of water has a high surface energy, it is readily contaminated (Drost-Hansen, 1965). Even minutely contaminated surfaces display certain unusual elastic characteristics such as the Plateau-Marangoni-Gibbs effect (Scriven and Sterling, 1960). In contrast to surface tension, the role of elasticity in free-boundary flows has not been widely recognized (Scriven, 1946). Yet elasticity is to be generally expected, since even in the laboratory the likelihood of a clean surface is remote (Davies and Rideal, 1963). In a natural stream surface contamination is a certainty.

Elastic properties of a contaminated surface can be attributed to local variations in surface tension (Whitaker, 1964) which exert a two-dimensional surface pressure,  $p$ , in the plane of the surface (Davies and Rideal, 1963)

$$p = \sigma_o - \sigma \quad (7)$$

In Equation 7  $\sigma_o$  is the surface tension of a clean portion of the surface and  $\sigma$  is the surface tension of a portion with adsorbed molecules. The surface pressure is always positive for water with adsorbed molecules. The forces resulting from these pressures are greater in regions of lower surface tension containing adsorbed molecules. Accordingly, the surface force is directed from a region of low surface tension to one of high surface tension.

In the case of turbulent fluids the surface pressure and associated force have a definite effect on the process of interfacial renewal (Rukenshtein, 1965). Eddies continuously bring bulk fluid to the surface and thereby increase the local surface tension. Adjacent surfaces have lower surface tensions and there is therefore a tangential force tending to resist surface renewals (Davidson and Cullen, 1959). The importance of the gradients rather than the absolute value of surface tension has been demonstrated experimentally (Davies and Kahn, 1965). Surface elasticity is apparently the most important property affecting the renewal of the surface (Berg and Acrivos, 1965).

An index of surface elasticity can be obtained by measuring the surface pressure,  $p$ , in conjunction with surface concentrations to produce force-area curves (Davies and Rideal, 1963). From these curves is obtained a two-dimensional compressional modulus (dynes per centimeter) relative to a clean surface. The value of the modulus depends on the state of the surface film and generally increases as surface tension decreases (Bikerman, 1958). The surface modulus as usually measured would be zero for the standard of a clean surface. However, even a clean surface of water should have an absolute resistance to surface compression due to its high elastic strength. Thus there should be a positive value for the two-dimensional compressional modulus for any water surface. For this discussion such a modulus is termed  $M_s$  and is used to reflect the surface elasticity of a water surface.

An eddy in the vicinity of the surface may approach the surface with a certain dynamic thrust which could cause a dynamic pressure proportional to the product of the fluid density,  $\rho$ , and the square of the eddy velocity,  $v$ . It is suggested herein that the resistance to this dynamic pressure comes from the elastic character of the surface region. If the compressional modulus reflects this character, the resisting pressure due to compression of a surface region of depth,  $x$ , would be  $M_s/x$ . The resistance must equal the dynamic pressure for a condition of surface stability; thus

$$\rho v^2 = \frac{M_s}{x} \quad (8)$$

An eddy, or portion of an eddy, traveling through the surface region of depth  $x$ , with velocity  $v$ , would have a residence time in the region proportional to  $x/v$ . The renewal rate,  $r$ , could then be proportional to  $v/x$ . Using Equation 8 we have:

$$r = C_1 \frac{v}{x} = \frac{C_1 \rho v^3}{M_s} \quad (9)$$

Levich (1962) presented an equation for gas transfer containing  $D_m^{0.5}$  which can be viewed as the case of Equation 6 with the coth term equal to unity (intense mixing). The remaining terms in his equation are equivalent to the surface renewal,  $r$ , and equal  $\rho v^3/\sigma$ , where  $\sigma$  is the surface tension. When this expression is compared with Equation 9, the similarity is noted, except that  $M_s$  appears in the latter equation while  $\sigma$  is contained in Levich's.

The eddy velocity may be proportional to the Kolomogoroff velocity factor,  $(\nu E_s)^{1/4}$ , in which  $\nu$  is the kinematic viscosity and  $E_s$  is the rate of dissipation of energy per unit mass of water near the surface. This proportionality,  $v = C_2(\nu E_s)^{1/4}$ , substituted in Equation 9 yields

$$r = \frac{C_1 C_3^3 \rho E_s^{3/4} \nu^{3/4}}{M_s} \quad (10)$$

The energy dissipated in the vicinity of the surface,  $E_s$ , should be proportional to  $E$ , the energy dissipated in the fluid as a whole. If  $E_s$  equals  $C_2 E$ , the resulting expression for  $r$  is

$$r = \frac{C_1 C_2^{3/4} C_3^3 \rho \nu^{3/4} E^{3/4}}{M_s} \quad (11)$$

The form of Equation 11 is similar to an equation previously proposed (Dobbins, 1964), with one difference. The latter equation contains surface tension as a parameter where Equation 11 has the modulus of compression,  $M_s$ . The significance of this difference is that values of  $M_s$  increase in the presence of surface-active materials, while surface tension values decrease. Thus Equation 11 is in qualitative agreement with reported observations that surface-active materials retard surface renewals. Quantitative evaluation of  $M_s$  in turbulent systems could lead to the use of Equation 6 for predicting the effects of surface-active materials on the absorption coefficient. This latter aspect is the subject of continuing research; however, for the work reported herein with distilled water,  $M_s$  is essentially constant.

It has been suggested (Dobbins, 1964) that the effective film thickness,  $L$ , might be related to the eddy size

$$L = C_4 \left( \frac{\nu^3}{E} \right)^{1/4} \quad (12)$$

where  $C_4$  is a constant which should be determined by the system.

The depth of surface region,  $x$ , as used in Equation 8, is not the same as the effective film thickness suggested in Equation 12. The former value represents the depth where resistance to surface overturn is extant. Indeed, this depth could be much less than the size of an eddy and could retard motion as a portion of an eddy moves through this region. If  $x$  were assumed to represent the film thickness, it would be inversely proportional to  $\nu^{1/2} E^{1/2}$ . Such an assumption would assign  $\nu^{1/2}$  to the denominator rather than  $\nu^{3/4}$  as in the numerator of Equation 12. In addition, the energy,  $E$ , would be raised to the  $1/2$  power instead of the  $1/4$  power. These changes would not permit the consistency in the experimental results demonstrated in this work.

The following relationship follows from Equations 11 and 12. The number of constants is reduced to one,  $C_5$ .

$$rL^3 = C_5 \frac{\rho \nu^3}{M_s} \quad (13)$$

This equation is independent of the energy dissipated and thereby provides a key relationship for experimental verification of the proposed equations. Equation 13 predicts that  $rL^3$  should be constant at a given temperature and that its temperature dependency is due mainly to the terms in the numerator.

### Experiment

**Apparatus and Procedure.** The apparatus, shown diagrammatically in Figure 1, was designed to allow determination of the amount of gas absorbed in a liquid by measuring the decrease in volume of the gas phase under constant pressure. A tube connects the absorption cylinder to a mercury manometer which contains an electrode to close a relay circuit when the mercury reaches a level of 763 mm. For a lower pressure, caused by absorption during operation, the circuit is broken

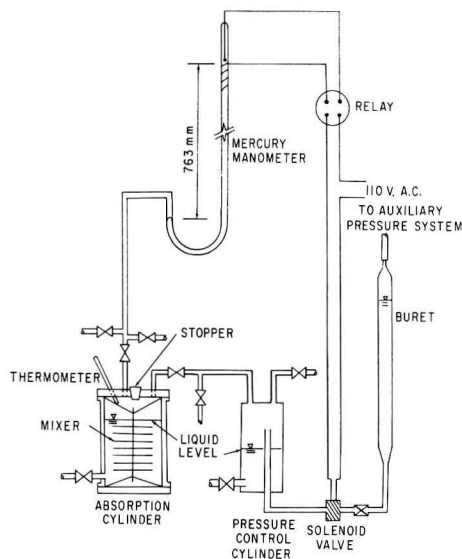


Figure 1. Experimental system

and the solenoid valve opens to allow water to be injected from the buret under auxiliary pressure into the pressure-control cylinder. The gas in the pressure-control cylinder is in free communication with the gas in the absorption cylinder and is compressed until the pressure returns to 763 mm. At this pressure the mercury comes in contact with the electrode and causes the solenoid valve to close. The increments of water added are as small as 0.05 cm, and equal the volume of gas absorbed during a very brief interval. The total volume of gas absorbed at any time is given by the reading of the buret. These readings are made at the completion of each injection and associated times recorded to 0.01 minute.

Figure 2 shows the absorption cylinder, which is a Lucite cylinder with flanged ends and removable top and bottom. A thermometer extends into the upper portion of the cylinder, which contains gas during the operating phase. The absorption unit is provided with a lattice mixer driven vertically in simple harmonic motion with a stroke of 2.5 cm, by a variable-speed motor. A rocker arm extends through the side of the absorption cylinder through a completely sealed fitting and connects to the drive mechanism. Mixer speeds may be set in the range of 3 to 200 oscillations per minute. The term "cover" used in this work refers to the depth of water above the upper mixer blade at the top of a stroke during an experiment.

The absorption cylinder, manometer, and pressure-control cylinder are set in water baths which provide controlled temperatures. The temperature in the absorption cylinder is recorded to  $0.01^\circ \text{C}$ ., with a variation during a run not usually exceeding  $0.10^\circ \text{C}$ . Corrections to the data are made for the volumetric changes in the enclosed gas caused by temperature variations during a run.

Before an experiment the entire system is filled with the gas to be used in the experiment. The gas is then forced from the system by admitting gas-free water, which is allowed to remain

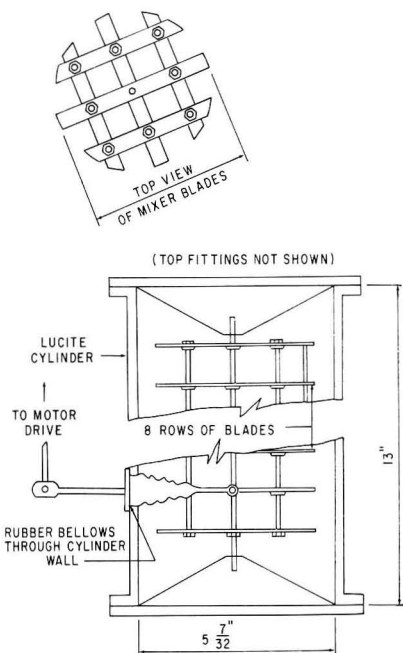


Figure 2. Absorption cylinder

until the desired temperature is reached. Gas is then introduced as the water is withdrawn from the cylinders to the desired operating levels. Distilled water was used for the majority of the experiments. A limited number of runs were made with tap water; however, no difference was noted and the results are presented together.

The course of absorption during a typical experimental run is shown in Figure 3 by curve *a-b-c-d*. The dashed axis is the reference for the liquid with no dissolved gas.  $Y_s$  represents the volume of gas absorbed at saturation. The solid axis shows the portion of the absorption curve used for computing the absorption coefficient. Point *a* indicates the possible dissolved gas in the liquid when it completely fills the absorption cylinder after repeated flushing of the system. During the interval from *a* to *b*, gas is introduced into the apparatus, and the water level and gas pressure are adjusted. Since the gas is in contact with the liquid, some absorption must take place. However, the amount of dissolved gas represented by point *b* is usually less than 10% of saturation. The buret reading is made at *b* and the mixer is started. The mixer is run for several minutes before an origin is established at *c* for computational purposes.

It is in the region *c* to *d* that data are obtained for determining the absorption coefficient. A first-order equation is fitted to this region, using the slope method suggested by Thomas (1937) to obtain the reaction constant,  $K$ , and the value of  $Y$  indicated in Figure 3. The value of  $K$  thus obtained from the experiments is related to the apparent liquid film coefficient,  $K_L'$ , through the liquid volume,  $V$ , and the surface area,  $A_0$ :

$$K_L' = \frac{KV}{A_0} \quad (14)$$

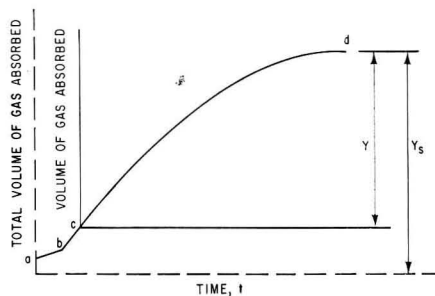


Figure 3. Course of absorption during experiment

**Results of Experiments.** Results of experiments conducted in an apparatus similar to that used for the present work have been reported (Dobbins, 1964). The results for helium and nitrogen (Figures 4 and 5) were obtained under four different conditions of mixer stroke and cover. From these results, it was concluded that any mixing condition that results in a certain value of  $K_L$  for nitrogen will also yield a definite value for helium. Thus, there is a consistent relationship between  $r$  and  $L$  which is independent of the mixing conditions which created them. This consistent relationship has been preserved in fitting the curves of Figures 4 and 5, although the curves represent a slight displacement from the original presentation.

The results of a series of experiments in which absorption coefficients for helium were obtained at various temperatures in distilled and tap water are presented in Figure 6. Figure 6 *a* was prepared from a limited number of runs conducted under intense mixing conditions with the upper mixer blade breaking the surface at the top of each stroke. In Figure 6 *b*, *c*, and *d*, results are presented for mixer speeds of 100, 73, and 33 r.p.m., respectively, with a 1-cm. cover and stroke of 2.5 cm. These latter conditions were also used to obtain the results shown in Figure 7 for nitrogen, oxygen, and argon in distilled water.

The data of Figures 6 and 7 are represented by straight lines on semilog paper, an observation reported by others (Elmore and West, 1961). The departure of oxygen and argon from the plotted straight lines of Figure 7 *a* and *b*, is due to their slight difference in diffusivity from that of nitrogen. Oxygen and argon values were not used in fitting the straight lines, but only to demonstrate that these other sparingly soluble gases followed the same temperature trend.

#### Analysis of Experimental Results

**Surface Areas.** The data of Figures 4 and 5 for distilled water can be represented linearly in the lower speed region for any condition of stroke and cover. The departure from linearity in each case occurred when the liquid surface was noted to begin to ripple. A similar observation was made by Downing and Truesdale (1955), who reported that the absorption coefficient was linear with mixer speed until a speed was reached which caused vortices.

When we assumed the departure from linearity of the curves in Figure 4 was due to an increase in area, ratios of the actual surface area to the horizontal projection of area were estimated by extrapolating the straight-line region and comparing this with the apparent values shown by the smooth curve. The



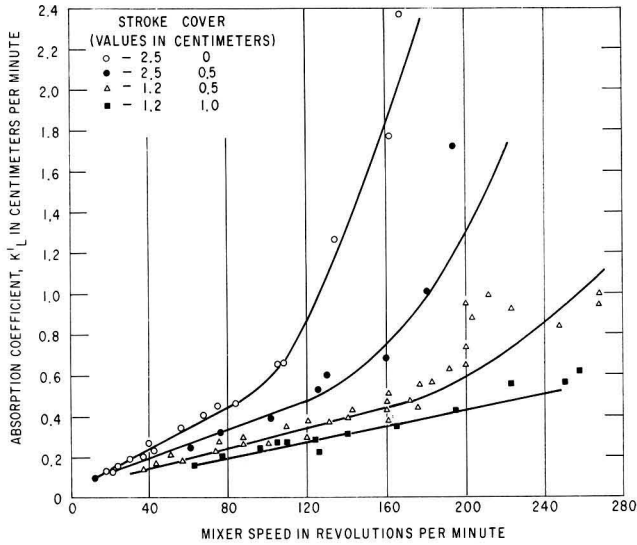


Figure 4. Absorption coefficients for helium

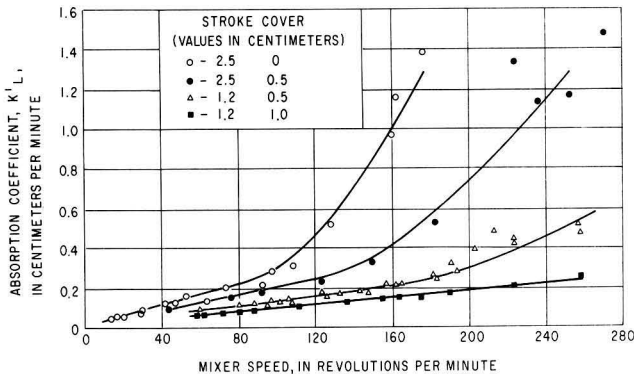


Figure 5. Absorption coefficients for nitrogen

ratios, designated by  $C_A$ , are plotted against mixer speed in Figure 8a for the three curves which departed from a straight line. This plot demonstrates concurrence with the results of Westerterp (1963), who reported that areas linearly depend on the agitation rate.

The  $C_A$  values obtained from each of the three curves have been plotted directly against the value of  $K_L'$  for helium in Figure 8b. When this is done, a single curve represents all the data. Similar results are obtained using the nitrogen data of Figure 5. Thus a given value of  $K_L'$  is always associated with a certain value of  $C_A$ , regardless of the mixing conditions which produced the value. It follows that there is a relationship between  $r$  and  $C_A$  such that as energy increases in a surface region there is a maximum  $r$  value that can be attained with a smooth surface. Further increase of energy increases  $r$ , but only with an accompanying increase in area. Energy is envisioned as being absorbed by the compressional elasticity of a surface within its "elastic limit." Increases of

energy imparted to a surface beyond this limit would cause marked deformations in addition to increased surface renewal frequency.

**Computation of  $r$  and  $L$ .** The experiments were conducted so that at given speeds and temperatures mixing conditions were identical for the measurement of the absorption coefficients for helium and nitrogen. Thus, from Equation 6, the value of the surface renewal frequency,  $r$ , and the film thickness,  $L$ , at a given mixing condition, can be computed by inserting the known values of  $K_L$  and  $D_m$  for each gas and solving the resulting two equations simultaneously. For helium and nitrogen, represented by subscripts 1 and 2, respectively, the following equations follow from Equation 6.

$$\frac{\coth \sqrt{\bar{\phi}}}{\coth \sqrt{\frac{D_1 \phi}{D_2}}} = \frac{K_1}{K_2 \sqrt{\frac{D_1}{D_2}}} \quad (15)$$

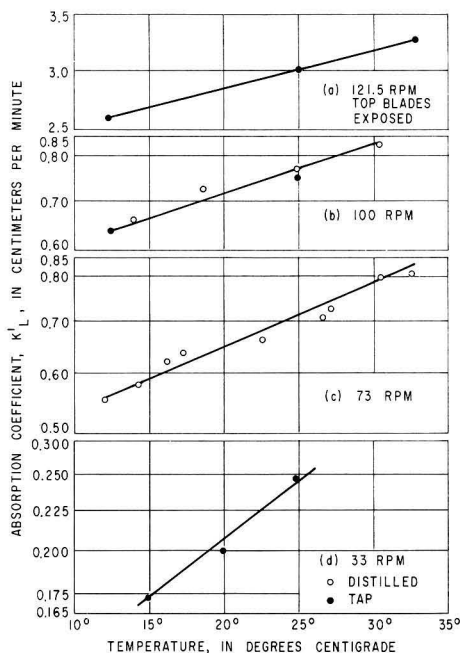


Figure 6. Absorption coefficients for helium

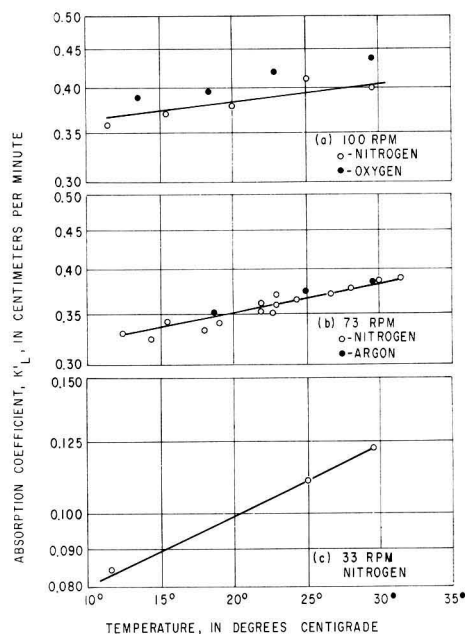


Figure 7. Absorption coefficients for nitrogen, oxygen, and argon

Table I. Diffusivities of Gases in Water<sup>a</sup>

(Values in sq. cm./sec.  $\times 10^5$ )

Temp., °C.	Nitrogen	Helium	Oxygen
10	1.40	4.09	1.59
15	1.63	4.76	1.85
20	1.88	5.49	2.14
25	2.16	6.30	2.45
30	2.46	7.16	2.79
35	2.77	8.08	3.14

<sup>a</sup> Selection of values presented in detail elsewhere (Metzger, 1965). 25°C. values for nitrogen and oxygen accepted as a mean of reported values. Helium value at 25°C. determined by using a ratio of helium to nitrogen of 2.92, which was obtained experimentally and is in accord with reported values. Diffusivities at other temperatures computed using Stokes-Einstein equation.

$$\sqrt{r} = \frac{K_1}{\sqrt{D_1} \coth \sqrt{\phi}} \quad (16)$$

$$L^2 = \frac{D_1 \phi}{r} \quad (17)$$

where

$$\phi = rL^2/D_1$$

If the apparent values of the absorption coefficient are used ( $K_1'$  and  $K_2'$ ), Equations 16 and 17 are equally valid but yield apparent values ( $r'$  and  $L'$ ). The apparent values can be related, using Equation 4, to true values as in:

$$r' = C_A^2 r \quad (18)$$

$$L' = L/C_A \quad (19)$$

The solution of Equations 15, 16, and 17 depends upon a knowledge of the diffusivities of the two gases used. In addition, the variation of diffusivity with temperature is desired. Unfortunately, there is some lack of agreement in the literature concerning this information. Under these circumstances, some of the experimental results were interpreted (Metzger, 1965) in conjunction with reported data to make a reasonable estimate of the values required. The values used in this work are presented in Table I.

Equations 16 and 17 were used to compute apparent and true film thicknesses and surface renewal frequencies using  $K_L'$  values for helium and nitrogen from the smooth curves of Figures 4 and 5. The values computed with data from the linear portions of the curves are true values. Apparent values, computed from data which departed from linearity, were corrected to true values by using the  $C_A$  values of Figure 8 *b* and Equations 18 and 19. These computations form the basis for the plots of Figure 9, in which the value of  $r$  is plotted against  $L$  and  $r'(L')^3$ .

The data of Figures 6 and 7 were also collected under identical physical conditions in order to compute values of  $r$  and  $L$ . Results of computations for  $r'(L')^3$ ,  $L'$ , and  $r'$  are plotted against temperature in Figure 10 *a*, *b*, and *c*, respectively. Apparent values have been presented because of the uncertainty of  $C_A$  at temperatures other than 20°C.

**Verification of Proposed Equations.** The range of computed film thicknesses shown in Figure 9 *a* compares with those reported by Bolin (1960), Kanwisher (1963), and Davis and Crandall (1930), who estimated a film thickness of  $3.5 \times 10^{-3}$ ,  $10 \times 10^{-3}$ , and  $40 \times 10^{-3}$  cm., respectively. These computed film thicknesses display a consistent relationship with the

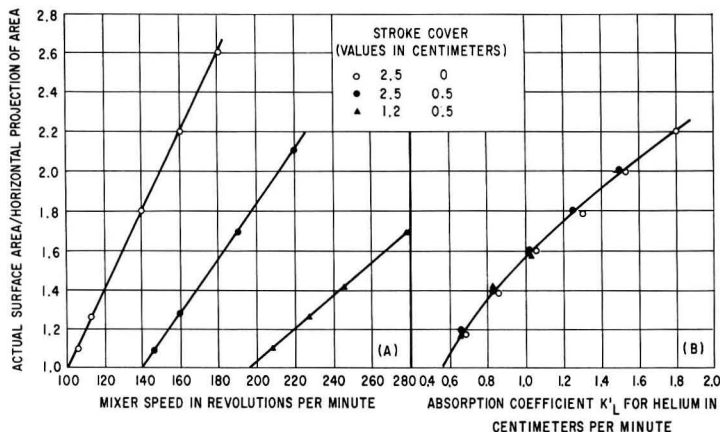


Figure 8. Ratios of actual surface area to horizontal production of area from helium data

surface renewal frequencies which is in accord with the proposed equations.

The values of  $r'(L')^3$  depicted in Figure 9 *b* remain constant, until the water surface begins to ripple, then begin to decrease. This decrease is due to an increase in surface area, since  $r'(L')^3$  is equal to  $rL^3/C_A$ . The coefficient,  $C_A$ , may then be computed from these curves in addition to the manner previously discussed. When this is done, the same values of  $C_A$  are obtained as previously shown in Figure 8. Thus for a given temperature and surface modulus,  $rL^3$  remains constant in accord with Equation 13.

Figure 10 *a* demonstrates that  $r'(L')^3$  has a consistent decreasing trend with temperature for each series. The 20° C. values for the three series will all yield an  $rL^3$  value of about  $81 \times 10^{-6}$  cc. per minute when surface area corrections are applied. If the same  $C_A$  factors were assumed to hold at other temperatures, all the data would be represented by a single line. The slope of the lines (or single line) representing the three series is the same as for the group  $\rho\nu^3$  as predicted by the numerator of Equation 13.

As for the denominator of Equation 13,  $M_s$  may also be temperature-dependent. However, if its dependency is of the order of the variation in surface tension due to temperature, any change in  $M_s$  would be masked by the larger change in  $\nu^3$ . It would appear that the group  $C_s/M_s$  can be considered nearly constant over the range 15° to 30° C. and that  $M_s$  is not strongly dependent on the system dynamics in distilled water. The validity of Equation 13 would therefore be established.

The effect of temperature on the film thickness is shown in Figure 10 *b*. These curves are in qualitative agreement with Equation 12, which predicts lower  $L'$  values for higher energies and a decrease in  $L'$  with the temperature for constant energy. Figure 10 *c* demonstrates the effect of temperature on  $r'$  and is in qualitative agreement with Equation 11. Correlation with either Equation 11 or 12 is not possible for the mixer data, since the value of  $E$  is unknown. However, these relationships can be used in Equation 6 to predict the effects of temperature on oxygen absorption.

**Effects of Temperature on Aeration.** The effects of temperature on the absorption coefficient for oxygen is often rep-

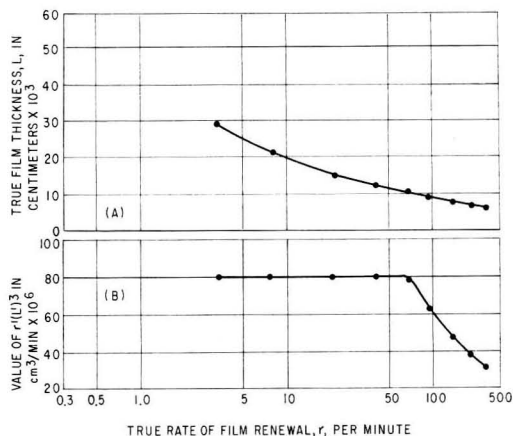


Figure 9. Relation of  $r$  to  $L$  and  $r'(L')^3$  computed from helium and nitrogen data

resented by an equation of the form  $K_T = ae^{bT}$ , where  $a$  and  $b$  are constants and  $T$  is temperature. The constant,  $b$ , may be obtained from the slope of a semilog plot of  $K_T$  vs.  $T$ . It is common to relate temperature effects to a value at 20° C.; thus  $K_T/K_{20^\circ} = (e^b)^{T-20}$ . When  $(e^b)$  is replaced by  $\theta$ , the equation takes the familiar form

$$K_T = K_{20}(\theta)^{T-20} \quad (20)$$

Equation 20 is not necessary when the film penetration model is used and, in fact, may be not entirely correct. It is presented to draw attention to the fact that the slope of each line of Figures 6 and 7 is related to  $\theta$ . These slopes become steeper as the mixer speed decreases, indicating that the effects of temperature are more marked at the lower conditions of turbulence. There is no single value of  $\theta$  which can represent the entire spectrum of mixing conditions. Therefore,  $\theta$  would have to be a variable in Equation 20, constant values being applicable only over certain ranges of turbulence.

**Table II. Effects of Temperature on Absorption Coefficient for Oxygen**

Temp., °C.	Low Intensity Mixing			High Intensity Mixing		
	10	20	30	10	20	30
$D_m$ , sq. cm./sec. $\times 10^5$	1.59	2.14	2.79	1.59	2.14	2.79
$r$ per min.	0.37	0.30	0.25	122	100	83
$L$ , cm. $\times 10^3$	67	55	45.5	12.2	10.0	8.3
$\sqrt{rL^2/D_m}$	1.34	0.84	0.55	4.37	2.83	1.85
$\coth \sqrt{rL^2/D_m}$	1.15	1.46	2.00	1.00	1.01	1.05
$\sqrt{D_m r}$	0.0188	0.0196	0.0204	0.34	0.36	0.37
$K_L$ , cm./min.	0.0216	0.0287	0.0408	0.340	0.364	0.388
Ratio		1.330	1.420		1.070	1.065
$\theta$		1.029	1.036		1.007	1.006

In addition to the variations in slope with mixer speed, the nitrogen slopes are flatter than the helium slopes for comparable mixer speeds and covers. This observation is in accord with the film penetration model, which predicts that the gas of higher diffusivity would be more affected by temperature changes. While the film penetration model will automatically account for this, the value of  $\theta$  in Equation 20 would have to be different for each gas, in addition to depending upon the turbulence.

Table II has been prepared to illustrate how Equation 6 can account for temperature changes in oxygen absorption. Consistent values of  $r$  and  $L$  were selected for a condition of high and low mixing intensity. The effects of temperature were assumed to be due mainly to the  $\nu^{3/4}$  term in Equations 11 and 12. The rate of dissipation of energy,  $E$ , was considered to be unaffected by temperature changes (Kozinski and King, 1966), which would seem appropriate for rivers. It is seen from the table that the film penetration model predicts an increase in  $K_L$  for oxygen with temperature which depends on the turbulence and the temperature. The computed values of  $\theta$  range from 1.036 for very gentle mixing to 1.006 for rapid mixing characterized by distortion of the surface. Intermediate mixing conditions yield values between these limits and demonstrate a continuous variation in  $\theta$ . The various values of  $\theta$  reported in the literature are in agreement with the latter observations.

Gameson, Vandyke, and Ogden (1958) conducted aeration experiments at weirs and reported a  $\theta$  value of 1.015. In a slowly stirred system, Downing and Truesdale (1955) reported 1.0212 and indicated lower values for higher stirring rates. Elmore and West (1961) absorbed oxygen at low mixing intensities and observed a value of 1.0241, while in higher intensity experiments it was 1.0226. Kozinski and King (1966) reported data which result in a value for  $\theta$  of 1.036 for low surface renewal frequencies.

The importance of recognizing that the liquid film coefficient,  $K_L$ , is a more basic parameter than the reaeration coefficient,  $K_2$ , may be illustrated by the work of Elmore and West. They adjusted their experimental conditions to produce a  $K_2$  value which was nearly the same as found in Tennessee streams. The natural streams have depths of about 3 to 10 feet (Churchill *et al.*, 1962) while the mixer depth was about 1 foot. This means that the  $K_L$  produced in the mixer was approximately one third to one tenth that found in the streams. To adjust the mixer to comparable stream conditions based on

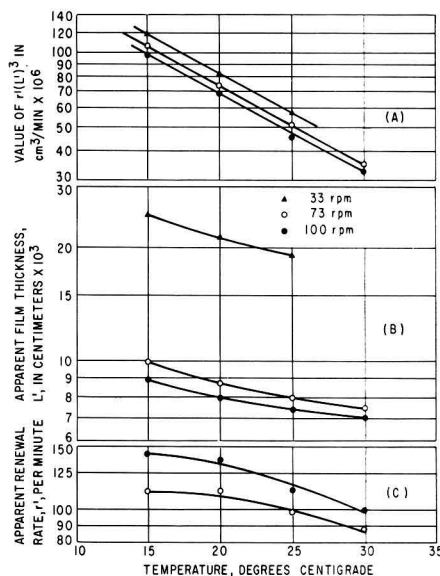


Figure 10. Relation of temperature to  $r'(L')^3$ ,  $L'$ , and  $r'$  computed from helium and nitrogen data

$K_L$ , a  $K_2$  value of three to ten times the stream value should have been used. At this higher mixing intensity a lower value of  $\theta$  would probably be found and would be more appropriate for the natural streams considered.

### Conclusions

A rational physical model for the absorption of low-solubility gases into turbulent liquids is based on the concept that an interfacial liquid film is in a continuous state of random renewal. Proposed equations for the rate of renewal and thickness of the interfacial film were purportedly verified in laboratory experiments. When these equations are used in the basic model for gas absorption, it predicts effects of temperature on oxygen absorption which are in agreement with values reported in the literature.

## Nomenclature

- $A_0$  = horizontal projection of surface area  
 $A_s$  = actual surface area  
 $C_A$  = ratio of  $A_s$  to  $A_0$   
 $C_L$  = concentration of dissolved gas in fluid bulk  
 $C_0$  = concentration of dissolved gas in liquid at initial time  
 $C_s$  = concentration of dissolved gas at saturation  
 $D$  = dissolved oxygen deficit  
 $D_m$  = molecular diffusivity  
 $D_1$  = molecular diffusivity of helium  
 $D_2$  = molecular diffusivity of nitrogen  
 $E$  = rate of dissipation of energy per unit mass for flow as a whole  
 $E_s$  = rate of dissipation of energy per unit mass in vicinity of surface  
 $H$  = depth  
 $K$  = first-order equation parameter (base  $e$ ) per time interval  
 $K_L$  = liquid film absorption coefficient  
 $K_L'$  = apparent liquid film absorption coefficient  
 $K_1$  = liquid film absorption coefficient for helium  
 $K_2$  = liquid film absorption coefficient for nitrogen, and re-aeration constant (base  $e$ )  
 $L$  = liquid film thickness  
 $M_s$  = modulus of compression at surface  
 $n$  = exponent  
 $r$  = frequency of surface renewal  
 $t$  = time  
 $T$  = temperature in degrees Centigrade  
 $v$  = velocity  
 $V$  = volume of liquid aerated  
 $x$  = distance  
 $Y$  = first-order equation parameter  
 $Y_s$  = volume of gas dissolved at saturation  
 $\nu$  = kinematic viscosity  
 $\phi$  = ratio of  $rL^2$  to  $D_1$   
 $\rho$  = mass density  
 $\theta$  = constant  
 $\sigma$  = surface tension

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## Thin-Layer Chromatographic Method for Estimation of Chlorophenols

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■ A rapid, nonsophisticated analytical method is used for estimation of certain chlorophenols known to affect the flavor of water adversely at the parts per billion level. The two-directional thin-layer chromatographic technique employs two supplementary reagents, aminoantipyrine and silver nitrate, both of which provide independent sensitivities of less than 1 p.p.b. The technique has been applied to surface waters before and after treatment and should be useful to investigators studying the effects of water treatments. ■

A rapid, selective, and highly sensitive method was needed for determination of chlorophenols in water. This type of compound is known to affect the flavor of water adversely at parts per billion concentrations.

A number of procedures and modifications for determining phenolics in water have appeared in the literature (Ettinger and Ruchhoff, 1948; Ettinger *et al.*, 1951; Lyttan, *et al.*, 1946; Murray, 1949; Rosenblatt *et al.*, 1954; Schmauch and Grubb, 1954; Simard *et al.*, 1951).

The method developed is a two-directional thin-layer chromatographic procedure. Extraneous petroleum ether ex-



tractives from water are separated from the chlorophenols in one direction with benzene, and chromatographed in another direction with an alkaline acetone solution. Two separate chromogenic agents are used for detection. The method is specific for chlorophenols and has a sensitivity of 0.1  $\mu\text{g.}$  using silver nitrate and 0.5  $\mu\text{g.}$  using the 4-aminoantipyrine reagent. Little or no interference is caused by inorganic compounds, color, or turbidity. The method gives excellent reproducibility and has been successfully applied to surface waters before and after primary and secondary treatments.

#### Procedure

**Reagents.** Acetone, analytical reagent grade.

Aluminum oxide G with gypsum binder, Warner Chilcott.

Petroleum ether, pesticide quality, Matheson, Coleman and Bell or equivalent.

Mobile solvent I, benzene, ACS grade.

Mobile solvent II, 6 ml. of 1*N* NaOH plus 94 ml. of acetone.

Sodium sulfate, granular, anhydrous, ACS grade.

Sodium hydroxide, ACS grade, 1*N* solution in H<sub>2</sub>O.

4-Aminoantipyrine, Eastman Kodak No. 6902, 2% in acetone, freshly prepared.

Potassium ferricyanide, ACS grade, 8% in water, stored in refrigerator.

Silver nitrate, analytical reagent grade. Dissolve 0.5 gram of AgNO<sub>3</sub> in 5 ml. of distilled water, add 100 ml. of 2-phenoxyethanol (practical), and make up to 1 liter with acetone. Add 3 drops of 30% hydrogen peroxide, mix, and transfer to low actinic glass bottle.

Orthophosphoric acid, 85%, analytical reagent grade.

Chlorophenols, obtained from Eastman Kodak.

**Extraction.** Acidify a 1-liter sample of water with phosphoric acid to a pH of approximately 1.5 and place in a 2-liter separatory funnel. Extract the water with four separate 100-ml. portions of petroleum ether (Faust and Aly, 1965). Combine the ether extracts in a 600-ml. beaker and evaporate to ca. 5 to 10 ml. on a steam bath with the aid of a gentle current of air. Dry the concentrated extract over sodium sulfate, quantitatively transfer to a 15-ml. graduated centrifuge tube, and evaporate to 0.1 ml. Spot this solution on a thin-layer plate.

**Chromatography (TLC-Sandwich Assembly).** Prepare aluminum oxide TLC plates as described by Kovacs (1963) and dry at 120°C. for 1 hour in a forced draft oven. Scrape a one-half inch border of adsorbent from all sides of the plate as indicated in Figure 1. Spot the sample in as small an area as possible, approximately  $\frac{3}{4}$  inch from the lower right-hand corner (Figure 1).

Assemble the thin-layer plate sandwich and allow mobile solvent I to ascend 3 to 4 inches up the plate as shown in Figure 1. Remove the plate and allow it to dry. If mobile colored material is not removed from the sample spot, repeat the benzene wash until the spot is sufficiently clean. Some samples may require three to four benzene washings.

Spot chlorophenol standards of 0.05, 0.1, and 0.5  $\mu\text{g.}$ , ahead of the benzene front, and in line with the previously spotted sample (see Figure 1). Reassemble the sandwich and run mobile solvent II perpendicular to the direction of benzene. Allow it to ascend  $\frac{1}{2}$  inch from the top of the plate, disassemble the sandwich, and dry the plate. Develop chromatograms at room temperature for 30 to 40 minutes.

Spray the silver nitrate reagent heavily and dry in a forced

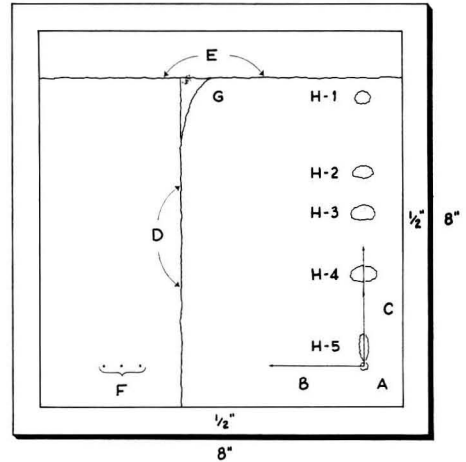


Figure 1. Thin-layer chromatography plate

- A. Sample spot placed  $\frac{3}{4}$  inch from each side of adsorbent layer
- B. Direction of benzene wash
- C. Direction of alkaline-acetone mobile solvent
- D. Benzene solvent front
- E. Alkaline-acetone solvent front
- F. Standard spots, 0.05, 0.1, and 0.5  $\mu\text{g.}$
- G. Extraneous extractives
- H. 1. *m*-Chlorophenol  
2. 2,4-Dichlorophenol  
3. 2,4,5-Trichlorophenol  
4. 2,4,6-Trichlorophenol  
5. Pentachlorophenol

Table I. *R<sub>f</sub>* Values and Sensitivity for Five Chlorophenols

Compound	<i>R<sub>f</sub></i> (Solvent Front)	Sensitivity, ( $\mu\text{G./Liter}$ )	
		AgNO <sub>3</sub>	Antipyrine
<i>m</i> -Chlorophenol	0.94	0.1	0.5
2,4-Dichlorophenol	0.71	0.1	0.5
2,4,5-Trichlorophenol	0.62	0.1	0.5
2,4,6-Trichlorophenol	0.42	0.1	0.5
Pentachlorophenol	0.09	0.5	...

Table II. Recovery of 2,4-Dichlorophenol

Amounts added, $\mu\text{G./L.}$	Raw river water	Carbon-filtered water	Per Cent Recovery			Distilled water
			Well water	Before treatment with ClO <sub>2</sub>	After treatment with ClO <sub>2</sub>	
0	...	...	...	...	...	...
0.1	75	85	80	85	85	95
0.5	80	90	80	85	85	90
1.0	80	90	85	90	90	100
5.0	80	95	90	95	95	100
10.0	90	95	95	95	95	100
Av.	81	91	86	88	88	97

draft oven (80°C.) for 1 to 2 minutes. Then expose the plate to ultraviolet light for 15 minutes in a chamber similar to that described by Kovacs (1963). Spots will appear light to dark brown.

If the concentration of any chlorophenol is found to be less than 0.5 µg. per liter with the AgNO<sub>3</sub> reagent, extract a larger sample for confirmation by the less sensitive 4-aminoantipyrine reaction. When the concentration by AgNO<sub>3</sub> detection indicates more than 0.5 µg. per liter, extract a duplicate sample and chromatograph on a separate plate in the manner previously described. Spray the 4-aminoantipyrine reagent moderately heavily and dry the plate with the aid of a warm air flow. Lightly spray the plate with 1*N* sodium hydroxide, again dry with warm air, and spray moderately with ferricyanide solution. The chlorophenols, with the exception of pentachlorophenol, will appear as pink to red spots against a yellow background.

**Results.** Table I shows the *R<sub>f</sub>* values and the sensitivity obtained for five chlorophenols with the two chromogenic agents used.

Table II shows the recovery obtained by petroleum ether extraction of various kinds of water fortified with 2,4-dichlorophenol at five levels of concentration.

Comparable recovery results were also obtained for the chlorophenols listed in Table I when they were added to the six kinds of water and at the levels of concentration shown in Table II. At below 1 µg. per liter recoveries ranged from 75 to 95%; above that level, from 80 to 100%.

#### Discussion

The method was evaluated using raw river water from the Delaware and Maumee Rivers, well water, surface waters before and after chlorine dioxide treatment, carbon-filtered water, and distilled water. Results on representative samples analyzed before and after fortification (Table II) indicate a recovery range of 75 to 100%.

The majority of extraneous extractives which react with silver nitrate were identified by gas and thin-layer chromatography. They were found to consist primarily of contaminants from the solvent and trace amounts of DDT and DDE and the esters of 2,4-D and 2,4,5-T. The extraneous extractives do not interfere with the detection of the chlorophenols, since they are separated by the benzene wash.

Extraction with either petroleum or ethyl ether resulted in comparable recoveries for the chlorophenols tested. However, petroleum ether is the preferred solvent because it extracts less extraneous organic matter from water and therefore its extracts can be more readily spotted.

Of the several types of Al<sub>2</sub>O<sub>3</sub> used, the one selected gave the best separation and sensitivity for the chlorophenols.

The time and temperature for activation are critical.

Variations of 5° to 10°C. will produce erratic results. Once the plates are activated, cooled, and placed in a desiccator they can be used. However, aging in the desiccator for one or two days will increase sensitivity.

Depending upon the type of water to be analyzed, an extract equivalent to 1 to 2 liters can be spotted. The extract of 1 liter of raw river water will normally be the maximum amount which can be spotted. In such instances this procedure will provide a sensitivity of 0.1 µg. per liter for the chlorophenols. Usually an extract of 2 to 5 liters of water which received primary or secondary treatment can be applied to a plate to provide a sensitivity range of 0.02 to 0.05 µg. per liter.

#### Summary

A highly sensitive, rapid, and selective thin-layer chromatographic method is used for the determination of *m*-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol in raw and treated water.

These compounds can be readily detected below levels at which they may affect the flavor of water. Concentrations of 0.1 µg. per liter or more can be determined using 1-liter samples and the silver nitrate reagent. Confirmation of 0.5 µg. per liter or more can be readily achieved with the 4-aminoantipyrine reagent, again using 1 liter as the sample size. The use of two separate chromogenic reagents, one of which responds to phenols and the other to the halogen, in conjunction with thin-layer chromatography, provides a very high degree of specificity.

The method is rapid, offers good recovery and reproducibility, and has been found satisfactory for all samples of waters encountered.

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# Effects of Gaseous Air Pollutants on the Response of the Thomas SO<sub>2</sub> Autometer

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■ A study was made of the quantitative response of the Thomas SO<sub>2</sub> Autometer to gases that might coexist with SO<sub>2</sub> as air pollutants. These gases included NO<sub>2</sub>, NO, HCl, Cl<sub>2</sub>, NH<sub>3</sub>, and HF. The gas mixtures were prepared dynamically at the parts per million level by a flow mixing method to a high degree of accuracy. Syringe pumps were used to add small quantities of pure gases to a large volume air stream. The effects of NO<sub>2</sub>, NO, and HF on the SO<sub>2</sub> reading were small, but HCl, NH<sub>3</sub>, and Cl<sub>2</sub> gave significant response.

In working with the Thomas Autometer (Thomas *et al.*, 1946) for monitoring SO<sub>2</sub> levels in air pollution studies, it was desired to know to what degree pollutants other than SO<sub>2</sub> would interfere with the instrument reading. Both the newer 0-2 p.p.m. SO<sub>2</sub> and the older 0-5 p.p.m. SO<sub>2</sub> full-scale range instruments were being used in these studies. The principle on which the Autometer operates is the measurement of the increase in electrolytic conductance of a dilute H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> solution by the absorption and oxidation of SO<sub>2</sub> to form additional H<sub>2</sub>SO<sub>4</sub>. Since conductance measurements are not specific, any gas that is absorbed and forms ions could be measured as SO<sub>2</sub>.

The gaseous pollutants that are commonly present with SO<sub>2</sub> in the atmosphere are the oxides of nitrogen (NO and NO<sub>2</sub>), ozone, hydrocarbons, and carbon monoxide (Jutze and Tabor, 1963). Of these only NO and NO<sub>2</sub> would be expected to interfere with the Autometer reading, since they form HNO<sub>3</sub> on absorption. The possibility of interferences produced by inorganic particulates such as sodium chloride and calcium carbonate is worthy of mention. Many Autometer field installations employ a simple glass wool plug filter in the air sample line, which effectively removes most of these particulates. Those that do pass through could be absorbed to produce an erroneously high SO<sub>2</sub> reading. The magnitude of the error thus produced has not been determined, but should be a promising area of future study. Olivo (1958), also working with the Autometer, reported that the readily absorbed gases were SO<sub>2</sub> (98 to 99%), HCl, HF, and NH<sub>3</sub>. The less readily absorbed gases were nitrogen oxides, CO<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub>SO<sub>4</sub> aerosol. The interference produced by H<sub>2</sub>S was given as 1 p.p.m. H<sub>2</sub>S  $\cong$  0.006 p.p.m. SO<sub>2</sub>. In a study of the effects produced by HCl, Yocom *et al.* (1956) found that the Autometer response to this gas was 1 p.p.m. HCl  $\cong$  0.45 p.p.m. SO<sub>2</sub>. The quantitative effects of nitrogen oxides on the SO<sub>2</sub> readings of the Autometer have not been reported previously.

Nitrogen oxides have been reported to interfere with SO<sub>2</sub> measurements made by several analytical methods. Moore, Cole, and Katz (1957), in a comparative study of batch analyses by the fuchsin-formaldehyde colorimetric and conductometric methods, found that the presence of NO<sub>2</sub> gave low results with the colorimetric method. When the colori-

metric readings were corrected for the NO<sub>2</sub> present as determined independently by the Saltzman method, the conductometric and colorimetric values for SO<sub>2</sub> agreed closely. In another laboratory study, Terraglio and Manganeli (1962) reported that NO<sub>2</sub>-ozone mixtures interfered with the West and Gaeke (1956) colorimetric, iodometric, and acidimetric methods for SO<sub>2</sub> determination. High values were found with the acidimetric and iodometric methods, while low values resulted with the colorimetric method. The addition of sulfamic acid to the absorbing solution used in the West and Gaeke method was reported to minimize the effects of NO<sub>2</sub> on the SO<sub>2</sub> values obtained (West and Ordoveza, 1962). However, a loss of SO<sub>2</sub> could occur due to the pH effect of the sulfamic acid if such samples were not analyzed promptly. Hochheiser *et al.* (1966) concluded that there was no consistent relationship among SO<sub>2</sub> data obtained by the West and Gaeke, hydrogen peroxide, and conductance methods from several geographical locations because of the variable amounts of interfering substances present.

The fact that the Autometer uses an acidified hydrogen peroxide absorbing reagent of pH 4.4 suggests that the absorption of acid gases such as CO<sub>2</sub>, H<sub>2</sub>S, and the nitrogen oxides would be small. However, the absorption of SO<sub>2</sub> proceeds rapidly to completion, because the SO<sub>2</sub> is removed from the reaction zone by the peroxide oxidation to sulfate. This process also produces two hydrogen ions per molecule of SO<sub>2</sub> absorbed, which adds significantly to the reagent conductance. The oxidation step is specific to SO<sub>2</sub>, and the over-all Autometer response to SO<sub>2</sub> is many times greater than that of the nitrogen oxides. It is desirable to have an analytical method for SO<sub>2</sub> that is completely unaffected by the presence of other contaminants. Until this method is developed, it is necessary to know what the likely errors are in the currently used methods and to correct the SO<sub>2</sub> values obtained accordingly.

## Experimental

A number of experiments were thus done to determine the quantitative response of the Autometer when the air sample contained variable amounts of specific air pollutants. SO<sub>2</sub>, NO, NO<sub>2</sub>, HCl, Cl<sub>2</sub>, NH<sub>3</sub>, and HF were studied by themselves or in combination with definitely known SO<sub>2</sub> levels. The general approach was to meter the pure gas or gases into the sample stream and to observe the Autometer responses. Syringe pumps were used to feed the pure gases as described in a previous paper (Kuczynski, 1963). This was an improvement on the method reported by Saltzman (1955), in that "gas-tight" syringes were used to hold pure gases, thus precluding the necessity of making prior dilutions. The responses to SO<sub>2</sub>, NO<sub>2</sub>, and NO were determined with both the 0-2 and 0-5 p.p.m. SO<sub>2</sub> Autometers. The responses to the other gases studied were determined on the 0-5 p.p.m. SO<sub>2</sub> Autometer only.

**Sample System.** The air sample was drawn through a series arrangement of glass tubing, illustrated in

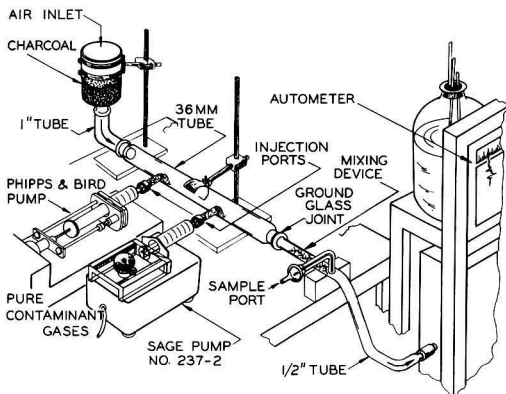


Figure 1. Gas-mixing system

Table I. Comparison of SO<sub>2</sub> Levels Generated by Pump and Syringe Method with Colorimetric West and Gaeke Method

Pump Setting	Calcd. SO <sub>2</sub> Concentration, P.P.M.	Av. Colorimetric Concentration, P.P.M.
Phipps and Bird		
D32	1.08	1.06
D16	2.12	2.14
E12	3.36	3.42
Sage pump, Serial No. 2197		
0.40	1.63	1.61
1.00	4.01	4.05

Figure 1, by the suction pump of the Autometer. Room air was drawn through a filter composed of 2 inches of charcoal (Fisher No. 5-685, 6-14 mesh), contained in an inverted vertically mounted polyethylene bottle from which the bottom had been cut off. The filter provided a low and stable base line for the Autometer and was recharged with fresh material every 2 to 3 days of operation. After passing through the filter, the air entered a mixing tube comprised of a section of 31-mm. i.d. tubing about 20 inches long. Several injection ports of 8-mm. tubing were sealed onto the mixing tube for the addition of the pure gases. These ports were filled loosely with glass wool and were closed with No. 12 rubber serum caps. A tube of 1/2-inch diameter and about 72 inches long connected the mixing tube directly to the Autometer inlet. A sample port of 2-mm. capillary tubing terminated with a No. 12-2 ball and socket joint was located in the 1/2-inch line to permit the collection of gas samples for analysis by other methods. Upstream of this sample port, a random arrangement of pieces of glass rod fused together was inserted in the sample line to disrupt laminar flow and to complete mixing of the gas components prior to sampling. The 1/2-inch tubing was connected to the 31-mm. mixing tube with a ground-glass joint to minimize absorption of the reactive gases used.

The time required for the Autometer to reach a stable reading with SO<sub>2</sub> was about 1/4 hour × p.p.m. level, much longer than the 212 seconds reported by Sanderson, Penner, and Katz (1964) in a study of Autometer response to short fumiga-

tion periods. This was probably due to the large volume of the sample system used in the present study.

**Method of Establishing Gas Concentration.** A dynamic flow mixing method was used for the preparation of the gas concentration of this study. The air flow through the sample system was adjusted to be 20 cu. feet per hour or 5.66 × 10<sup>6</sup> ml. per hour as measured with a wet-test meter (Precision Scientific Co., Chicago, Ill.). Pure gases were metered into the air stream with syringe pumps at rates of 0.57 to 12.8 ml. per hour. The approximate gas concentrations thus produced were calculated by taking the ratio of pure gas flow to air flow rates:

$$\text{P.p.m.} = \frac{\text{pure gas flow rate, ml./hr.} \times 10^6}{5.66 \times 10^6 \text{ ml./hr.}} = 1.77 \times \text{ml./hr.} \quad (1)$$

Independent checks of the SO<sub>2</sub> concentrations developed by the flow mixing method were made by the colorimetric West and Gaeke method. The procedure as modified by Hochheiser (1965) was used. Since charcoal-filtered air was used, the possibility of interference from nitrogen oxides was negligible. The average values of from five to ten determinations at each SO<sub>2</sub> level are given in Table I. It was necessary to correct the colorimetric values obtained for the volume of additional air drawn through the sampling system by the pump used to collect the colorimetric sample. Since this additional flow was 400 ml. per minute, and the normal flow through the system was 9439 ml. per minute, the correction factor was:

$$\frac{9439 + 400}{9439} = 1.042$$

The SO<sub>2</sub> concentrations predicted by the flow method and found by the colorimetric method are compared in Table I. These data indicated that the gas concentrations produced by the pump and syringe method were sufficiently accurate for calibration purposes.

Two Sage, Model 237-2 (Sage Instrument Co., White Plains, N. Y.) pumps were used in which the delivery rate could be selected from a wide range by setting the speed control dial. A third pump was a Model No. 71-045 infusion pump (Phipps and Bird Co., Richmond, Va.) obtained several years ago and modified in our shop. The delivery rate was selected by inserting the proper gear rack in the drive mechanism. Several syringe types were used. Most of the work was done with two 10-ml. volume Hamilton No. 1010 (Hamilton Co., Whittier, Calif.) gas-tight syringes, modified by adding O rings of Viton (E. I. du Pont de Nemours & Co. trademark) material to the Teflon (E. I. du Pont de Nemours & Co., trademark) plunger to aid in forming a leak-proof seal. No. 27 gage needles, 0.5 inch long, were used with the Hamilton syringes, with the cleaning wires supplied inserted in the needles to limit diffusion further. A Pressure-Lok No. 306003 (Precision Sampling Corp., Baton Rouge, La.) 5-cc. syringe was used for the calibration of the 0-2 p.p.m. SO<sub>2</sub> analyzer. Exact delivery rates for the pump and syringe combinations were determined by weighing the quantity of ethylene glycol delivered in a known time interval at specific pump settings.

The gas concentrations could then be calculated using the syringe delivery rate data with Equation 1. It was necessary to add a uniform correction of 0.05 p.p.m. to the gas concentrations as calculated. With the syringes filled with pure

Table II. Summary of Test Results

Gas Added	Concn., P.P.M.	SO <sub>2</sub> Added, P.P.M.	Autometer Reading Less SO <sub>2</sub> Reading, P.P.M.		Gas Added	Concn., P.P.M.	SO <sub>2</sub> Added, P.P.M.	Autometer Reading Less SO <sub>2</sub> Reading, P.P.M.	
			SO <sub>2</sub> P.P.M.	SO <sub>2</sub> P.P.M.				SO <sub>2</sub> P.P.M.	SO <sub>2</sub> P.P.M.
<b>NO<sub>2</sub></b>					<b>HCl</b>				
0-5 p.p.m.	1.63	0	0.08	0.08	0-5 p.p.m.	1.63	0	0.43	0.43
Autometer	4.01	0	0.15	0.15	Autometer	2.85	0	0.90	0.90
	7.80	0	0.28	0.28		4.01	0	1.42	1.42
	11.56	0	0.36	0.36		0	1.08	1.12	0
	0	1.08	1.15	0		4.01	1.08	2.53	1.41
	11.56	1.08	1.43	0.28		0	3.36	3.48	0
	0	3.36	3.40	0		2.85	3.36	4.36	0.88
	11.56	3.36	3.65	0.25	<b>Cl<sub>2</sub></b>				
0-2 p.p.m.	1.63	0	0.04	0.04	0-5 p.p.m.	4.01	0	0.10	0.10
Autometer	4.01	0	0.13	0.13	Autometer	7.80	0	0.20	0.20
	7.80	0	0.29	0.29		11.56	0	0.29	0.29
	15.31	0	0.59	0.59		0	1.08	1.10	0
	0	1.06	1.09	0		2.85	1.08	1.38	0.28
	4.01	1.06	1.18	0.09		7.80	1.08	1.57	0.47
	7.80	1.06	1.29	0.20		11.56	1.08	2.05	0.95
<b>NO</b>						0	3.36	3.40	0
0-5 p.p.m.	1.63	0	0.03	0.03		1.63	3.36	3.70	0.30
Autometer	4.01	0	0.09	0.90		2.85	3.36	3.92	0.52
	7.80	0	0.18	0.18	<b>NH<sub>3</sub></b>				
	11.56	0	0.29	0.29		0	1.08	1.12	0
0-2 p.p.m.	1.63	0	0.05	0.05		1.63	1.08	0.55	-0.57
Autometer	4.01	0	0.09	0.09		2.85	1.08	0.28	-0.84
	15.31	0	0.36	0.36		4.01	1.08	0.23	-0.89
	0	1.06	1.06	0		7.80	1.08	0.30	-0.82
	1.63	1.06	1.08	0.02		11.56	1.08	0.38	-0.74
	4.01	1.06	1.12	0.06		0	3.36	3.43	0
	11.56	1.06	1.33	0.27		1.63	3.36	2.93	-0.50
<b>NO + NO<sub>2</sub></b>						7.80	3.36	1.17	-2.26
0-2 p.p.m.	0	0	1.06	1.07	0	11.56	3.36	1.19	-2.24
Autometer	0	1.63	1.06	1.08	0.01	15.31	3.36	1.25	-2.18
	2.12	2.19	1.06	1.06	0.08	22.79	3.36	1.29	-2.14
					<b>HF</b>				
						0	1.08	1.16	0
						11.56	1.08	1.08	-0.08
						22.79	1.08	0.86	-0.30

SO<sub>2</sub> and in place in an injection port of the mixing tube, but with the pump motor not running, an upscale shift in the base line of the Autometer was observed. This offset averaged 0.05 p.p.m. of SO<sub>2</sub> over several long-term runs and appeared to be independent of the volume of pure gas put into the syringe. This correction factor was presumed to arise from leakage or diffusion from the syringes. The fact that the sample system was operating at a negative pressure of about 0.5 inch of water could have contributed to the large apparent leakage effect observed. Since air would have replaced the pure gas lost by this process in the syringe, precautions were taken to purge and recharge the syringe with pure gas at least every 6 hours of use. Again from Equation 1, the flow equivalent of 0.05 p.p.m. was calculated to be 0.03 ml. per hour. After 6 hours at the lowest flow rate the gas remaining would still be about 96% pure, and would have only a minor effect on the gas concentration generated. This leakage effect

was assumed to take place whether or not the pump was running.

**Autometer Calibration.** The Autometers were brought to the proper operating condition as prescribed by the manufacturer (Leeds & Northrup Co., 1964). Previous to this, the conductivity cells had been removed and tested to ascertain the exact cell-constant values. The solution flow rate was measured over several 8-hour periods by collecting the output of the integrating cell chamber when it dumped. This volume averaged 194 ml. per hour at room temperature. When allowances were made for expansion of this volume to the 120°F. operating temperature of the analyzers and the volume lost by evaporation to the air stream, this solution flow rate was very close to the specific 198 ml. per hour or 3.3 ml. per minute. The calibration procedure described by Kuczynski (1963) was used.

A typical calibration run for the Autometers used is il-



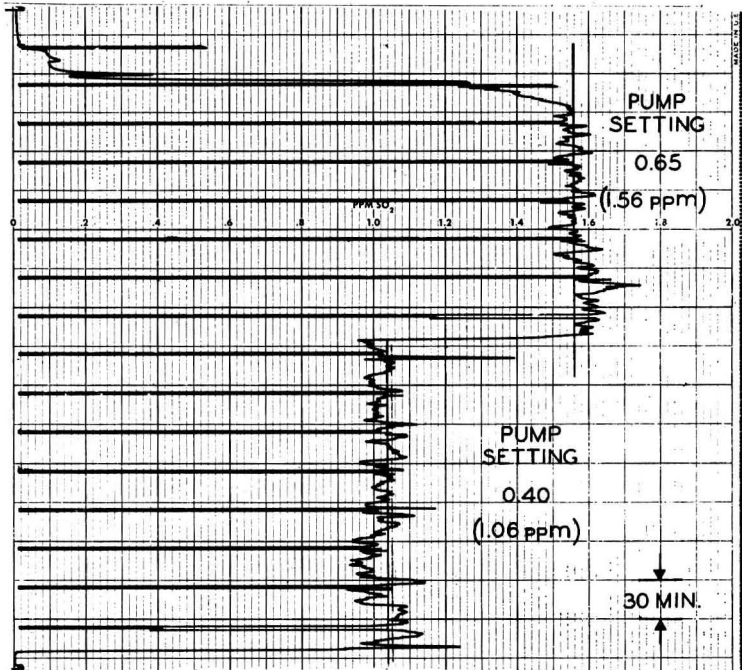


Figure 2. Typical calibration run

0-2 p.p.m. SO<sub>2</sub> Autometer  
Sage pump 2199  
Pressure-Lok 306003 syringe, 5 ml.

illustrated in Figure 2. This figure is included to show the response characteristics of the Autometer to the SO<sub>2</sub>-air mixtures prepared by the mixing system. It was concluded that the Autometers were adequately calibrated and would indicate SO<sub>2</sub> levels to within  $\pm 0.03$  p.p.m. of SO<sub>2</sub> of the true value.

**Tests with Other Gases.** Pure gases in cylinders of lecture bottle size were obtained from Air Products and Chemicals, Allentown, Pa., and the Matheson Co., East Rutherford, N. J. A syringe was filled with the gas under study, and the gas was added to the sampling system either by itself or in combination with SO<sub>2</sub> added from a second syringe and pump unit. In one test SO<sub>2</sub>, NO<sub>2</sub>, and NO were added, using all three syringes and pumps at the same time. The flow rates of the gases were varied to produce a wide range of concentration levels, and each level was maintained sufficiently long to give a stable reading with the Autometer.

#### Results and Discussion

The response data recorded as equivalent parts per million of SO<sub>2</sub> for the gases studied are given in Table II. Linear extrapolations of these data were used to derive the equivalent responses cited.

NO<sub>2</sub>. The effect of NO<sub>2</sub> by itself on the Autometer response was small:

$$1 \text{ p.p.m. NO}_2 \cong 0.036 \text{ p.p.m. SO}_2$$

probably because NO<sub>2</sub> was poorly absorbed by the Autometer

system. In the presence of about 1 p.p.m. SO<sub>2</sub>, the response was even smaller:

$$1 \text{ p.p.m. NO}_2 \cong 0.025 \text{ p.p.m. SO}_2$$

Apparently the SO<sub>2</sub> and NO<sub>2</sub> interacted to form less readily absorbable or ionizable products.

NO. Nitric oxide by itself produced the following equivalent response:

$$1 \text{ p.p.m. NO} \cong 0.024 \text{ p.p.m. SO}_2$$

In combination with 1 p.p.m. SO<sub>2</sub>, the NO response also was reduced slightly:

$$1 \text{ p.p.m. NO} \cong 0.022 \text{ p.p.m. SO}_2$$

NO<sub>2</sub> + NO. Adding two interfering gases in combination with SO<sub>2</sub> from separate syringes and pumps produced a substantially additive response. When 2.12 p.p.m. of NO<sub>2</sub> and 2.19 p.p.m. of NO were added to 1.06 p.p.m. of SO<sub>2</sub> an increase in the reading of 0.08 p.p.m. of SO<sub>2</sub> was observed. The above equivalences for the individual responses of NO<sub>2</sub> and NO in the presence of about 1 p.p.m. of SO<sub>2</sub> would have predicted an increased reading of 0.10 p.p.m. of SO<sub>2</sub>. A reproduction of the actual recorder chart made during this run is shown in Figure 3.

HCl. Significant responses were produced by HCl. At low levels of HCl (0 to 2 p.p.m.), it was found that

$$1 \text{ p.p.m. HCl} \cong 0.26 \text{ p.p.m. SO}_2$$

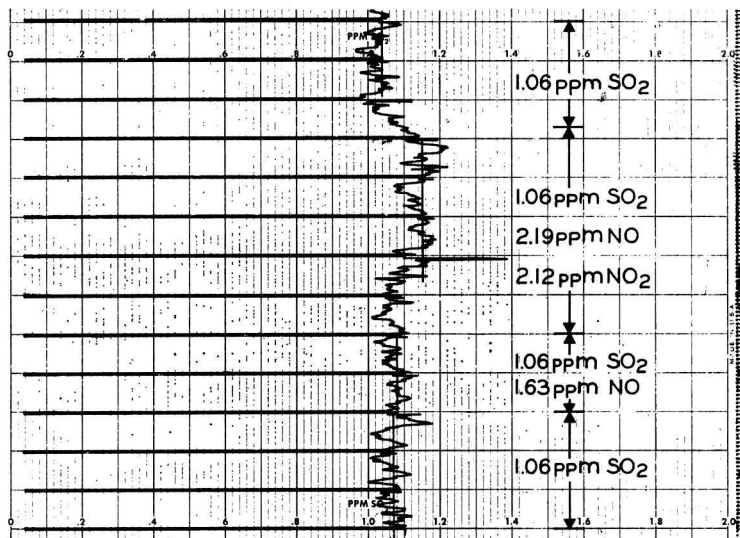


Figure 3. Response of Autometer to combined  $\text{SO}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$

However, at higher  $\text{HCl}$  levels (2 to 5 p.p.m.) the response was greater:

$$1 \text{ p.p.m. HCl} \cong 0.42 \text{ p.p.m. SO}_2$$

These values agreed well with those published by Yocom *et al.* (1956). The variation in response at the low and high  $\text{HCl}$  levels was attributed to differences in the conductance-concentration relationships of  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  solutions. The presence of  $\text{SO}_2$  had no measurable effect on the  $\text{HCl}$  response.

$\text{Cl}_2$ . Chlorine by itself gave only small Autometer response:

$$1 \text{ p.p.m. Cl}_2 \cong 0.025 \text{ p.p.m. SO}_2$$

When about 1 p.p.m. of  $\text{SO}_2$  also was present, response was:

$$1 \text{ p.p.m. Cl}_2 \cong 0.09 \text{ p.p.m. SO}_2$$

This enhancement was more evident when 3.5 p.p.m. of  $\text{SO}_2$  also was present:

$$1 \text{ p.p.m. Cl}_2 \cong 0.19 \text{ p.p.m. SO}_2$$

A possible explanation of this increased response when  $\text{SO}_2$  was present was the reaction of  $\text{SO}_2$  and  $\text{Cl}_2$  to produce  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ . It had been shown previously that  $\text{HCl}$  gave large responses with the Autometer.

$\text{NH}_3$ . Predictably ammonia with about 1 p.p.m. of  $\text{SO}_2$  gave a negative response because of the neutralization of the absorbing reagent:

$$1 \text{ p.p.m. NH}_3 \cong -0.34 \text{ p.p.m. SO}_2$$

After the equivalence point was reached, the addition of greater amounts of ammonia produced an increasing reading due to the conductance of the ammonia solution formed. A conductometric titration was actually performed by plotting the  $\text{NH}_3$  data of Table II and drawing straight lines through the series of points as shown in Figure 4. The lines connecting the points before and after the neutralization level intersected

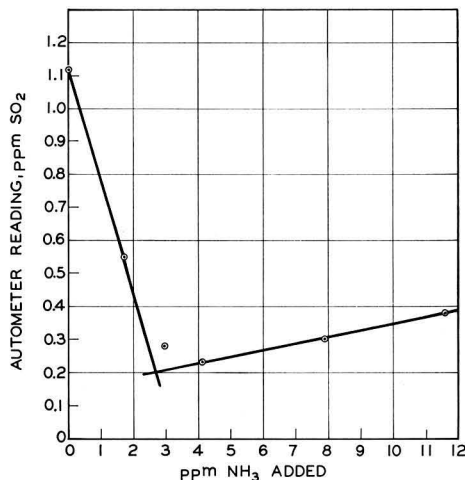


Figure 4. Autometer response to ammonia at 1.08 p.p.m.  $\text{SO}_2$

at 2.70 p.p.m. of  $\text{NH}_3$ . This amount of  $\text{NH}_3$  was equal to  $6.83 \times 10^{-5}$  eq. of  $\text{NH}_3$  per hour. The  $\text{SO}_2$  added would have produced  $5.80 \times 10^{-5}$  eq. of  $\text{H}_2\text{SO}_4$  per hour, and the absorbing solution would have contributed  $0.99 \times 10^{-5}$  eq. of  $\text{H}_2\text{SO}_4$  per hour ( $5 \times 10^{-5}N$ ). Thus the total  $\text{H}_2\text{SO}_4$  was  $6.79 \times 10^{-5}$  eq. per hour, which agrees closely with the  $6.83 \times 10^{-5}$  eq. per hour of  $\text{NH}_3$  found at the neutralization point. This indicated that the relative rates of  $\text{SO}_2$  and  $\text{NH}_3$  addition were at least consistent.

$\text{HF}$ . The response to  $\text{HF}$  was unusual. A slight negative effect was produced with  $\text{HF}$  by itself and in combination with  $\text{SO}_2$ . It was not known how much  $\text{HF}$  actually reached

the absorption column and measuring cell due to the reactivity of HF with the system components. Thus these response data are only qualitative in nature. A possible explanation of the negative response with HF could be the suppression of the ionization of H<sub>2</sub>SO<sub>4</sub> by the large amount of HF added.

### Conclusions

The SO<sub>2</sub> readings obtained with the Thomas Autometer are substantially accurate even when significant levels of NO and NO<sub>2</sub> also are present. This specificity for SO<sub>2</sub> in the presence of nitrogen oxides is due to the nature of the absorbing reagent and absorption system used.

Other gases such as HCl, Cl<sub>2</sub>, and NH<sub>3</sub>, although not considered to be universal pollutants, would cause significant errors in the SO<sub>2</sub> readings obtained with the Autometer and other conductance-type instruments.

The versatility of the flow mixing system used to prepare the parts-per-million gas mixtures of this study has been demonstrated. The system is simple and easy to use, and should be valuable whenever reactions involving parts-per-million gas mixtures are to be studied.

Thomas and Amtower (1966) in a recent paper described a gas-mixing technique and interference study very similar to the one described above. Their results on the effects of NO<sub>2</sub> on SO<sub>2</sub> conductance values were in general agreement with those reported here. A similar absorbing reagent but a different absorption device were employed, however. These authors reported difficulty in dispensing nitrogen oxides from syringes. Similar difficulties also were encountered in the pres-

ent work with nitrogen oxides. Nevertheless it was possible to obtain several hours' operating time before the needle became clogged. This time was sufficient to perform the tests reported.

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## COMMUNICATIONS

# Remote Sensing and Characterization of Stack Gases by Infrared Spectroscopy

## An Approach Using Multiple-Scan Interferometry

We have explored the feasibility of monitoring smokestack effluents by measuring the infrared emission spectra of the stack gases from a ground location remote from the stack. The results of the experiments indicate that such measurements can be carried out and offer a new approach to studies in air pollution.

The sensing instrument used was a Block Model 200 infrared interference spectrometer. The principles and methods of infrared interference spectroscopy have been described in detail (Low and Low and Coleman, 1966). The small optical system of the instrument was mounted on an 8-inch reflecting telescope, which served to limit the field of view of the instrument to a portion of the plume of a smokestack of a Rutgers power plant burning No. 6 bunker fuel. The interferometer-telescope combination was located approximately 600 feet from the plume.

The interference spectrometer covers the range 2500 to 250 cm<sup>-1</sup> in a scan of 1-second duration, with a resolution of approximately 18 cm<sup>-1</sup>. Successive scans can be added coherently and stored in a built-in computer core memory. The memory can function in a "subtract" as well as in an "add" mode, so that it is possible to correct spectra by sub-

tracting "background." Some typical spectra recorded on the same evening are shown in Figures 1 and 2. The ordinates are displaced to avoid overlapping.

Spectrum A of Figure 1 shows the relative emission of the sky near the smokestack, obtained at 6 P.M. The sky was slightly hazy but cloudless. The well-known "10- to 14-micron window" of the sky is prominent in spectrum A. The telescope was then pointed at the wispy, tenuous plume, and spectrum B was recorded. A series of bands due to the infrared emission of the stack gases is seen to be superimposed on the sky "background." When the background (spectrum A) was subtracted electronically from the total emission spectrum B, emission spectrum C resulted.

Figure 2 shows the results of a similar series of measurements. The spectra were recorded at 11 P.M., when the sky had become heavily overcast. The plume was barely visible, but appeared to be somewhat larger than that at 6 P.M. As shown in spectrum A of Figure 2 of the relative emission of the night sky, the atmospheric "window" had been decreased by the cloud cover, so that spectrum B of the total relative emission of the plume was only slightly modified when the correction for background was made to result in spectrum C.

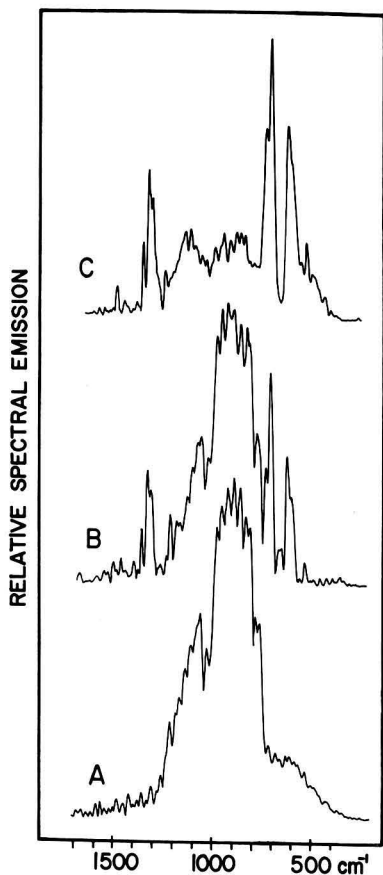


Figure 1. Infrared emission spectra of stack effluent

Spectra recorded at 6 P.M., each resulting from 50 scans

- A. Sky near plume
- B. Plume plus sky
- C. Plume only (sky "background"—i.e., spectrum A—subtracted from spectrum B)

Spectrum C shows a prominent, broad emission band in the 500- to 800-cm.<sup>-1</sup> region due to the emission of hot CO<sub>2</sub>. The band is split into two components by the narrower absorption band of cold atmospheric CO<sub>2</sub>. The assignment of the emission band marked *f* is uncertain at present; it is probably due to incompletely burned fuel. The noise level of the spectrum can be seen from the portion of the spectrum at wavenumbers higher than 1400 cm.<sup>-1</sup> Numerous minor bands of slightly or even appreciably greater intensity than noise are due to H<sub>2</sub>O. Also shown and marked are the infrared emission bands of SO<sub>2</sub> pollutant resulting from the combustion of the fuel.

The data obtained so far are qualitative in nature, and work is required to study the effects of atmospheric conditions, plume-to-instrument distance, and the like. However, the results of the above and similar exploratory experiments suggest the feasibility of the technique. Infrared spectra can be recorded from a position remote from the source of pollution, and the discharge of pollutants not observable by direct visual inspection can be detected. Significantly, this can be

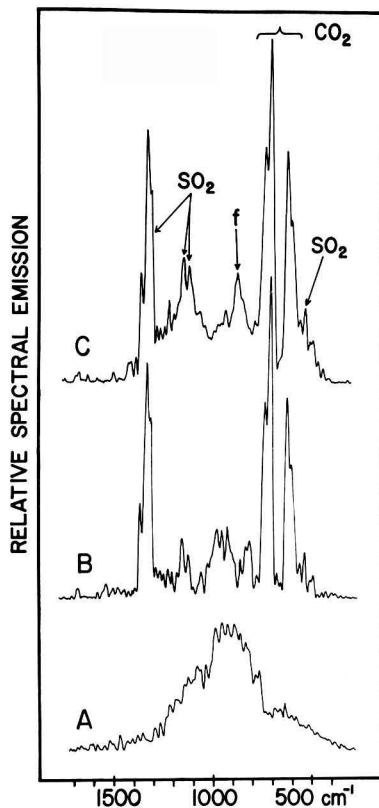


Figure 2. Infrared emission spectra of stack effluent

Spectra recorded at 11 P.M., each resulting from 100 scans

- A. Sky near plume
- B. Plume plus sky
- C. Plume only (sky "background"—i.e., spectrum A—subtracted from spectrum B)

done at night, when surveillance by other methods becomes difficult if not impossible. The method could thus become useful to monitor known sources, to inspect suspected sources, and to uncover previously unknown sources of pollution. The results thus point to a potentially valuable avenue of approach to various monitoring and detection problems in air pollution.

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# Evaluation of a Visual Color Comparator Method for Determination of Atmospheric Nitrogen Dioxide

In preliminary, widespread field surveys of atmospheric pollution concentrations, equipment for sampling and analysis that does not rely upon a source of a.c. electric power is advantageous. Low-volume battery-powered air pumps suitable for aspirating air samples through gas bubblers or filtration units and visual color comparators employing uniformly tinted glass filters mounted in a revolvable disk are commercially available. A method for measuring the concentration of oxidants in air by the phenolphthalein method using a visual color comparator has been developed (Haagen-Smith and Brunelle, 1958; Tintometer Ltd.). Because nitrogen dioxide is a common air pollutant and a satisfactory colorimetric method of analysis is available (Saltzman, 1954); U. S. Department of Health, Education, and Welfare, Public Health Service, 1965), it was thought desirable to apply this procedure to visual colorimetry using the visual color comparator. To our specifications the manufacturer of this apparatus prepared a color disk containing nine colored glass filters having appropriate spectral characteristics. This apparatus was evaluated in a comparison study of data obtained by use of the visual color comparator and data obtained spectrophotometrically. A ten-member untrained observer panel was used to obtain measurements by means of the visual color comparator.

## Experimental

**Apparatus.** A standard Lovibond Comparator with special NO<sub>2</sub> color disk, having glass filters corresponding to 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0 μg. of NO<sub>2</sub> gas complete with 10-ml. capacity 13.5-mm. diameter cuvettes, is available from Hayes G. Shimp, Inc., 866 Willis Ave., Albertson, L. I., N.Y. A Bausch and Lomb, Spectronic 20 spectrophotometer with 0.5-inch diameter test tubes was used in the spectrophotometric analysis.

**Reagents.** The diazotizing, coupling, and absorbing reagents used are the same as those described by Saltzman (1954). An NO<sub>2</sub> test solution (1 ml. to 10 μg. of NO<sub>2</sub>) was prepared from sodium nitrite. The empirically determined factor of 0.72 mole of sodium nitrite per mole of NO<sub>2</sub> gas was used.

**Procedure.** Azo dye sample solutions produced by reaction of diluted sodium nitrite test solutions and absorbing reagent were evaluated spectrophotometrically and by use of the visual color comparator. In the spectrophotometric method, absorbancy of the liquid samples was determined at 550 mμ and these data were converted to NO<sub>2</sub> concentration by reference to a calibration curve. NO<sub>2</sub> data were obtained by the visual color comparator method by visual matching of the color of the liquid sample and reagent blank against the color of stained glass filters. To accomplish this, the disk was revolved until the color filter matching the sample appeared. If the color of the sample lay between colors of the filters, the NO<sub>2</sub> concentration was estimated to the nearest 0.1 μg. by extrapolation.

## Results and Discussion

Measurements obtained by the observer panel using the visual color comparator were analyzed statistically, and the average value was compared to the NO<sub>2</sub> value determined spectrophotometrically (Table I). In the range of concentrations of interest, the average difference between results for these two methods is less than 17%; an exception occurs when the concentration of NO<sub>2</sub> of the liquid sample is less than 1.0 μg. per 10 ml. as determined spectrophotometrically, in which case the average difference is 27%, the lower values being obtained by the visual comparator method. NO<sub>2</sub> values determined with the visual comparator are within ±20% of the values obtained spectrophotometrically 95% of the time, except when the lowest color density filter is used. These data indicate that the visual color comparator is most suitable for analyses of liquid samples containing more than 1 and less than 7 μg. of NO<sub>2</sub>. If the method is applied to air analysis, sampling time or sampling rate should be gaged so that 1 to 6 μg. of NO<sub>2</sub> is collected.

## Conclusions

Standard colored filters prepared by the Tintometer Co. for use with the standard Lovibond Comparator are suitable for estimating atmospheric NO<sub>2</sub> concentrations if a deviation

Table I. Comparison between Visual Comparator and Spectrophotometric Methods for NO<sub>2</sub>

Test Solution No.	Spectrophotometric		Visual Comparator, NO <sub>2</sub> μG./ML. (10-Observer Panel)										Av. Difference between Methods, %	Statistical Decision, α% <sup>b</sup>			
	NO <sub>2</sub> , μg./10 ml.	NO <sub>2</sub> , p.p.m. <sup>a</sup>	1	2	3	4	5	6	7	8	9	10			No.	Range	Arithmetic mean
1	0.63	0.03	0.6	0.5	0.4	0.4	0.5	0.4	0.4	0.5	...	...	8	0.4-0.6	0.46	-27	<10
2	1.13	0.05	1.1	1.0	1.0	1.0	1.0	1.1	0.9	1.1	1.1	1.0	10	0.9-1.1	1.03	-9	>95
3	1.67	0.07	1.6	1.5	1.3	1.4	1.4	1.2	1.4	1.4	1.5	1.4	10	1.2-1.6	1.41	-16	>95
4	2.11	0.09	2.2	2.0	...	2.0	1.9	1.8	2.0	2.0	1.8	1.7	9	1.7-2.2	1.93	-9	>95
5	3.25	0.14	3.5	3.0	3.0	3.1	3.2	3.2	2.9	3.1	3.2	3.0	10	2.9-3.5	3.12	-4	>95
6	4.20	0.19	5.1	5.0	4.9	4.2	4.8	4.8	4.9	4.2	4.2	4.2	10	4.2-5.1	4.63	+10	>95
7	5.27	0.23	6.0	6.0 <sup>f</sup>	5.9	5.8	5.8	6.0	5.9	5.9	5.8	5.5	10	5.5-6.0	5.86	+11	>95
8	6.18	0.27	7.1	7.0	7.0	6.8	7.1	7.1	7.0	7.1	7.5	6.5	10	6.5-7.5	7.02	+14	>95

<sup>a</sup> For a 12-liter air sample.

<sup>b</sup> Given samples of size NO<sub>2</sub>, one expects estimated value from visual comparator method to fall within range of spectrophotometric value ±20%, α% of time.



of  $\pm 20\%$  from results obtained with the spectrophotometric method is tolerable. The visual color comparator method should be useful in preliminary field surveys over a wide area when short-term measurements of air pollution are desirable and electric power is at a premium. If air sampling is conducted with battery-powered air pumps, both sampling and analysis are independent of an outside source of power.

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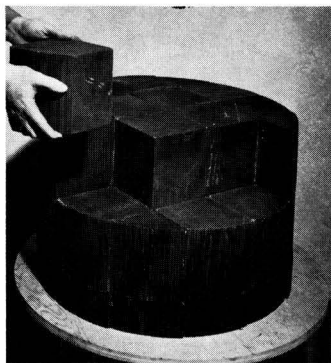
# NEW PRODUCTS DIGEST

## Pyrodecomposition

Cesspool waste, consisting of easy-to-pump, finely dispersed organic and inorganic solids in water (about 5% solids and 95% water), can be destroyed in the form in which it is collected. The new pyrodecomposition system, Model SF-4, has a rated capacity of 6720 gallons per week. No primary or secondary treatment is needed—the waste is consumed in the equipment by a process involving pyrolytic cracking, oxidation, and ionization. Pickands Mather & Co. 61

## Nitric Acid Abatement

Honeycombed ceramic blocks with a microscopic coating of palladium are used in a pollution abatement system for a nitric acid manufacturing process. The palladium catalyst covering the large surface area of the ceramic honeycomb permits the relatively low temperature reaction of oxides of nitrogen with any commonly available fuel,



eliminating the typical reddish-brown fumes of nitric acid from the stack and producing sufficient recoverable energy to make the plant essentially self-sustaining. Engelhard Industries, Inc. 62

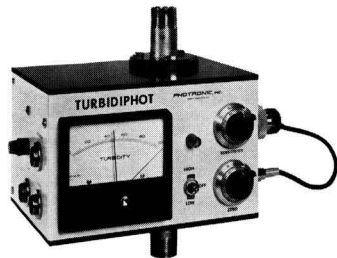
## Portable Water Lab

A portable water laboratory, using the Millipore filter method of water analysis, can be used by sanitary engineers

and field workers to conduct laboratory-type tests of drinking water in the field. The new kit makes possible a direct count of coliform organisms in large water samples in about 18 hours. The kit includes a variety of laboratory apparatus, enough filters and other expendable materials to conduct 100 tests, and facilities for sterilizing the filter holder assembly with bactericidal formaldehyde gas. Millipore Filter Corp. 63

## Turbidity Meter

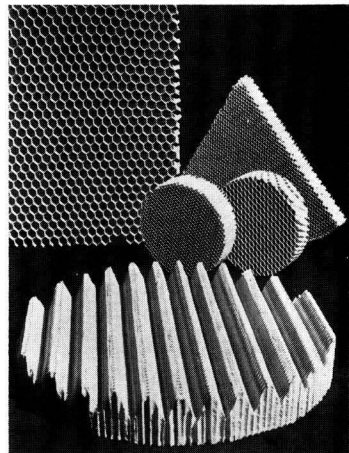
A new control instrument is available for continuous and automatic turbidity measurements in process streams. Turbidiphot Model 200 includes a new dual-detection system, which is based on absorption and low-angle scattering principles. The device has a rugged sampling chamber for direct in-line installation that, in most cases, permits the unit to operate without process pressure reduction. The new model has a built-in fail-safe mechanism and can



be fitted with high- and low-limit alarm contacts. For highly corrosive uses a sampling chamber made of Hastelloy C is available. Photronic, Inc. 64

## Ceramic Honeycomb

High-performance ceramic honeycomb, available in alumina and mullite compositions, has some unusual advantages in catalytic processing, combustion equipment, and in fume abatement devices. Torvex ceramic honeycomb has a high peripheral surface-area-to-volume ratio, good thermal stability, and black body thermal radiation characteristics.



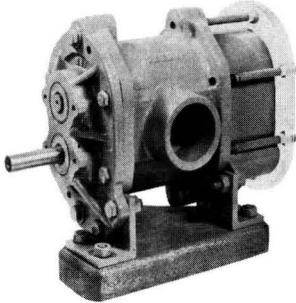
It is highly refractory and chemically inert to a wide range of materials. The honeycomb has high temperature stability (to 1500° C.) and, because of its low flow resistance and large catalytic area, is an excellent support for precious metal catalysts. These catalysts can be used as catalytic gauzes supported by the honeycomb, or the precious metals can be dispersed on the large surface area of the product. Torvex has been used in the abatement of nitric acid and hydrocarbon solvent fumes. E. I. du Pont de Nemours & Co. 65

## Versatile Colorimeter

An a.c.-operated, direct-reading colorimeter, which has separate meter scales calibrated for 45 different tests in the water and waste analysis field, is available. Separate meter scales for each test are included in the machine. These scales are inserted in the meter case and readings are made directly in p.p.m. or pH. The device includes a stabilizer transformer that gives freedom from line voltage variations and warmup takes less than a minute. The colorimeter comes with eight color filters, two sample bottles, a full set of meter scales, methods manual, and molded plastic carrying case. A battery model is also available. Hach Chemical Co. 66

## Vacuum/Pressure Transfer

Two new rotary positive blowers for continuous service and low-pressure small-volume applications where minimum space and weight considerations are important are available. Model 162, designed for low-speed use, and Model 163, designed for moderate-speed use, can be used for vacuum or pressure



transfer in septic tank waste disposal, aeration in activated sludge package plants, pneumatic conveying of bulk materials, and cake blowing. The

blowers can be used with either side or vertical connections and are driven by either a direct-connect electric motor or a V-belt. Dresser Clark. 67

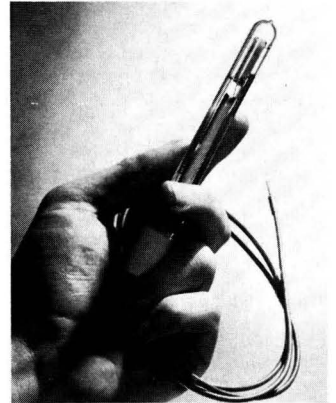
## Battery-Operated pH Meter-Recorder

Designed to record pH in rivers, process systems, and municipal and industrial effluents, analytical Model 30 pH meter-recorder is battery powered for portability. A nickel-cadmium battery powers the recorder for 48 hours and needs only 10 hours for recharging. Capable of providing a continuous and permanent record of final plant effluent, the recorder uses no ink. An a.c. line-operated version is also available. Analytical Measurements, Inc. 68

## Slow Electrodes

A new dual-glass junction general-purpose electrode can be used for continuous process applications and for contaminant-sensitive applications where frequent refilling of the electrode

cavity or electrolyte leakage are problems. The electrolyte flow rate in the new reference electrodes is between 0.5 and 3 microliters per hour compared with a slow-flow rate of 4 to 7 microliters per hour in electrodes commonly available. The new electrode has an output stability of  $\pm 0.5$  millivolt, a temperature range of  $-5^{\circ}$  to  $90^{\circ}$  C., and a 30-inch lead. Fisher Scientific Co. 69



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## CONTAMINATION ANALYSIS AND CONTROL

By JAMES L. DWYER, Director of Engineering Research,  
Millipore Filter Corporation, Bedford, Massachusetts  
1966/352 pages/\$15.00

This book offers a comprehensive guide to the practices of industrial particulate analysis and control. The sources and physical characteristics of these contaminants are described along with the most recent analytical techniques and the process control tools employed by modern industry. These basic techniques for detecting and controlling contaminants are simple and generally applicable. The author examines the following major subjects in depth: particles and droplets in gases; properties of aerosols; aerosol sampling; particles in liquids; properties of liquid suspensions; liquid sampling, sampling analysis; contaminants on surfaces; contamination control of airborne particulates; control of contaminants in liquids; and cleaning of surfaces.

## PARTICLES IN THE ATMOSPHERE AND SPACE

By RICHARD D. CADLE, National Center for Atmospheric Research, Boulder, Colorado  
1966/400 pages/\$10.00

One of the only books available dealing with fine particles in our universe, this work brings together in one volume information which has been scattered through a voluminous literature covering such subjects such as air pollution, astronomy, cloud physics, meteorology, radioactive fallout, and "space science." The author describes the nature, sources, and behavior of particles in the earth's atmosphere and on the surfaces and in the atmospheres of other planets. All aspects of radioactive fall-out are covered in a highly significant chapter.

## PARTICLE SIZE: Theory & Industrial Applications

by RICHARD D. CADLE

1965/416 pages/\$16.50

An excellent companion volume to the above, this book thoroughly covers the practical importance of particle size in terms of applications in a number of chemical and process industries. Broad in scope, it examines the basic physics of the action of fine particles dispersed both in exterior and interior environments.

## WATER AND ITS IMPURITIES

By THOMAS R. CAMP, Consulting Engineer, Camp, Dresser and McKee, Boston, Massachusetts

1963/368 pages/\$18.00

A thorough reference for those directly concerned with the design of works to solve the various manifestations of water pollution. This presentation of scientific information in sanitation engineering is unique in that it coordinates the physical, chemical and biochemical properties of water and its impurities in terms of the total environment—a perspective necessary to the development of water (and wastewater) control.

## WATER TREATMENT FOR INDUSTRIAL AND OTHER USES, Second Edition

By ESKEL NORDELL, The Permutit Company, New York, N.Y.

1961/608 pages/\$12.00

An exhaustive, practical reference on the conditioning and treatment of water supplies for industrial and domestic uses. Enlarged and rewritten, this second edition has been hailed by reviewers as one of the most authoritative books on the subject ever published.

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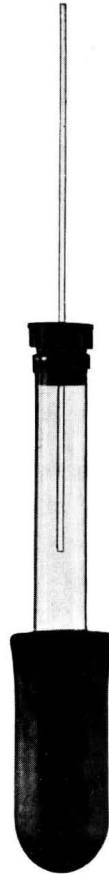
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Volume 1, Number 1, January 1967 83

### Automotive Antismog Unit

Similar to larger elements widely used in high-temperature industrial furnaces, a tiny igniter element made of a high-temperature cermet consisting mainly of molybdenum disilicide can be used in automobile after-burner type ex-



haust smog eliminators. The cermet elements, although as fine as 0.020 inch in diameter, are reliable and long lived. Operating at temperatures as high as

3000° F., these devices are used to burn hydrocarbons and carbon monoxide from car exhausts. U-shaped heating sections ranging in size from  $1/64$  to  $3/8$  inch can be made in appropriate lengths and in different configurations to meet the needs of limited space and tight wiring. Kanthal Corp. 70

### Submersible System

A four-element submersion-type water quality data collection system can be used for area surveys, research, and other monitoring uses in water systems. The sensors continuously measure the dissolved oxygen content, pH, conductivity, and temperature of water to depths of 25 feet. The newly developed dissolved oxygen and conductivity sensors have removable thermocompensators. The membrane of the dissolved oxygen sensor is an integral part of the polarographic cell. The system includes a submersible pump to provide a steady flow of water to the sensors. A spring-loaded pressure bellows is used in the pH reference electrode to assure uni-

directional flow of the reference solution. Each sensor is connected with a strip-chart recorder and includes integral zero and span adjustments and zener power supply. Honeywell, Inc. 71

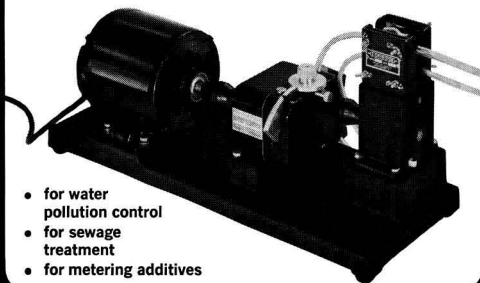
### Pumps and Filters

Newly designed corrosion-resistant reinforced epoxy pumps have excellent corrosion and erosion resistance, high strength-to-weight ratio, surface smoothness, high controllability, nonmagnetic, nongalling, and dimensional stability. Eight sizes are available—from 5 to 800 gallons per minute and heads to 300 feet—and are designed to conform to AVS proposed standards for centrifugal pumps. Also available is a new filter system that is corrosion resistant to abrasives, and such other typically corrosive solutions as those high in chlorides, fluoroborates, sulfuric acid, and cyanide. The filters can handle abrasive solutions at the rate of 50 to 2700 gallons per hour, filtering materials ranging between 1 to 150 microns. Sethco Pump Co. 72

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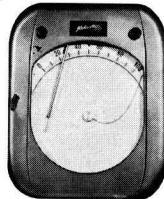
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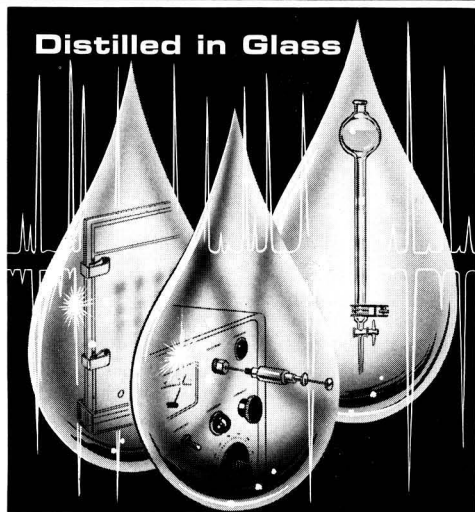
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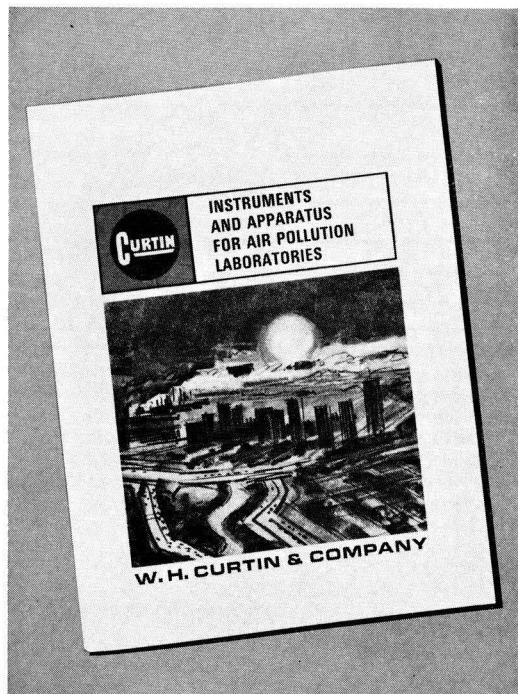
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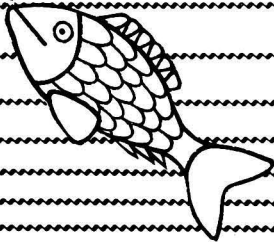


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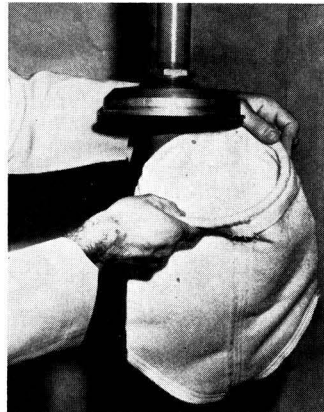


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filter bags are made of felts made of viscose, nylon, or polypropylene fibers. The regular molded adapter is suitable for service in alkali, solvent, and mild acid systems operating at temperatures up to 250° F. Adapter heads for strong acid service are available. AFCO Filter Products. **73**

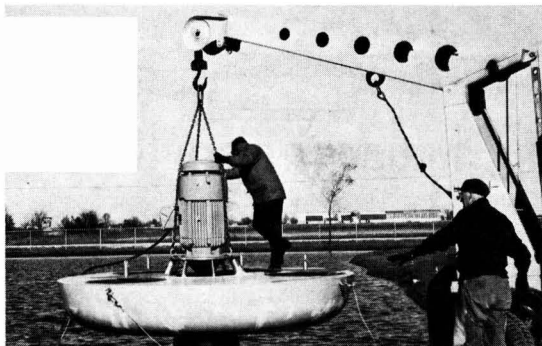
## Contaminant Analysis

Chemical processors are invited to submit samples of chemical processing fluids for a free contaminant analysis. The service is designed to aid processors in solving filtration problems in all types of fluid applications, such as solids recovery or removal of salts, pigments, and precipitates and such problems as are related to carbon removal in decolorization, catalyst recovery, and other filtering applications. After analysis of the contaminants, suggestions will be made for the most adequate and economical method of solving filtration problems. Chemical processors should obtain analysis data forms before sending their samples for analysis. Liquid Filter Corp. **74**



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### Potable Water

A new process using deionizer equipment produces potable water (350 p.p.m.) from ground and surface waters having 800 to 3000 p.p.m. of dissolved salts. The Sul-biSul process is currently demineralizing brackish water in a special demonstrator-pilot plant. Elgin Softener, Inc. 76

### Facility Leasing

Industry can lease a complete water or waste water treatment facility in a program that covers consulting engineering fees and all construction costs. The program, providing a complete operating facility on a long-term lease basis, can also cover any structures or plant piping required to complete the treatment facility with the construction being performed by a contractor of the user's choice. Gulfstan Corp. 77

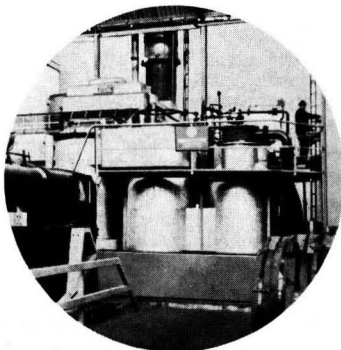
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### Pickle Liquor Cleanup

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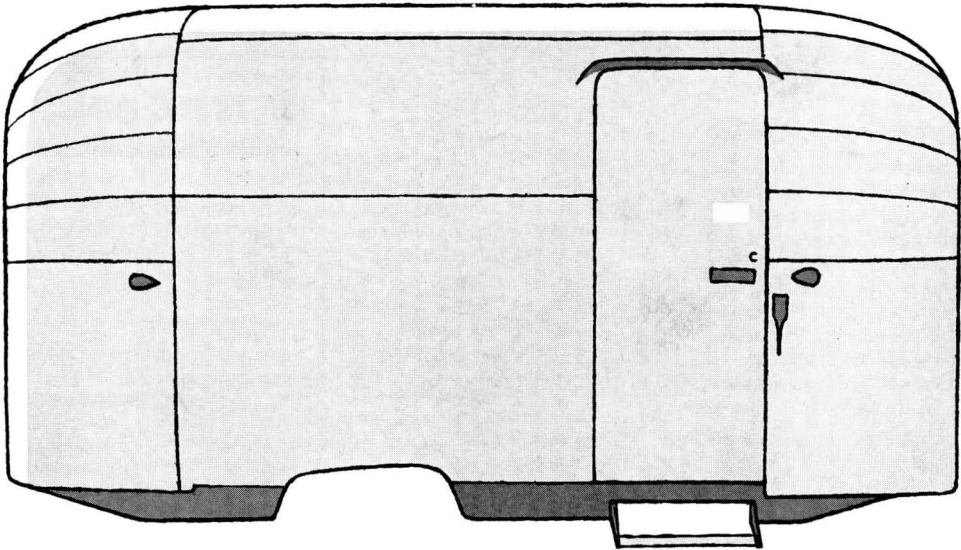
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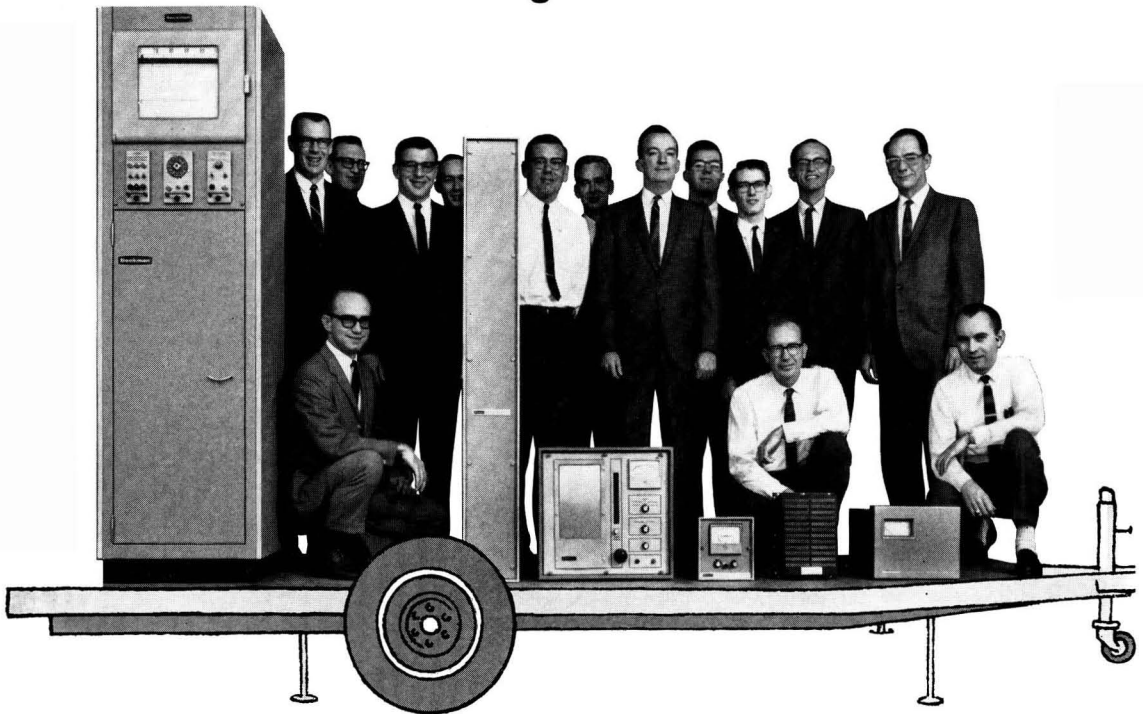
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**Activated carbon.** An 8-page bulletin describes the use of granular activated carbon for tertiary treatment of sewage and waste water, and for taste and odor removal from water supplies. The bulletin includes photographs, process flow sheets, plant efficiency data, and cost lists of an actual installation. Bartlett-Snow-Pacific. **81**

**Water quality.** A 16-page brochure discusses the effective management of water resources on the basis of accurate and continuous monitoring of the various characteristics that affect water quality. Included is a discussion of permanent and semipermanent systems and submersible systems for short-term survey work or where water sampling presents a problem. Honeywell, Inc. **82**

**Water treatment.** An 8-page bulletin describes water treatment equipment and processes available to the industrial, power, municipal, chemical, and industrial waste treatment markets. In addition to listing technical papers available on the general subject, the bulletin also briefly discusses ion exchange, condensate treatment, clarification, filtration, hot process systems, deaerating heaters, heat recovery and adsorption systems. Graver Water Conditioning Co. **83**

**Filtration glossary.** This 84-page glossary defines terms used in the filtration industry and explains how these terms are used. It includes both the precise and scientific definitions as well as many colloquial or coined terms that are common parlance in the field. About one third of the booklet is devoted to a

wide variety of tables and graphs that are useful to those working in any area where filtration is a part of the operations. Fram Corp. **84**

**Wet scrubbers.** This 24-page bulletin contains a great deal of information about all the basic types of wet scrubbers used for the removal of noxious gases, corrosive mists, and entrained solids. Included are operating schematics, basic design drawings, and engineering specifications. Comparisons of operating costs and performance characteristics of various types of wet scrubbers are made. Ceilcote Co. **85**

**Water treatment plants.** Two reports on the design of new water treatment facilities at Greenwich, Conn., and Phoenix, Ariz., are available. The reports describe the overall treatment facilities and highlight the use of special blowers in providing diffused air for the aeration systems of the sewage plants. Fuller Co. **86**

**Soluble silicates.** A 12-page bulletin covers the treatment of raw and waste waters with soluble silicates. The bulletin discusses the use of silicates as coagulants in many different areas and under many different conditions. Included in the bulletin are suggestions for small-scale tests, the preparation of laboratory stock solutions, and a nomograph for the preparation of activated silica sols. Philadelphia Quartz Co. **87**

**Gas chromatograph.** An 8-page brochure gives detailed illustrations and descriptions of Model 850 Prepkromatic automatic preparative gas chromatograph. The instrument separates and collects pure components for a multitude of scientific needs. The brochure also lists accessories for the new device. Nester/Faust Manufacturing Corp. **88**

**Surfactants.** A product bulletin and samples of a new family of low-foaming, biodegradable, nonionic detergents, emulsifiers, and wetting agents is avail-

able. Generically, the materials are described as acylated oxyethylated polyols. The bulletin includes product descriptions and information on the physical properties, physical performance data, and biodegradability. Charts showing detergency performance and control of bacterial growth are included. Millmaster Onyx Corp. **89**

**Process analyzers.** A 44-page booklet describes a line of process pH analyzers, ORP analyzers, electrodes, electrode chambers, and accessories. The booklet features the Model 900 process pH analyzer, including photographs and specifications of two versions of this instrument. Other portions of the bulletin deal with pH operating theory, industrial application data, and a bibliography of reference material on the theoretical and practical aspects of continuous pH measurement. Beckman Instruments, Inc. **90**

**Technical journal.** The Department of Health, Education, and Welfare, which sponsors the translation and publication in English of the West German technical journal, *Staub-Reinhalung Der Luft* (Dust-Clean Air Maintenance) reminds people working in the field of air pollution about the existence of the publication. Made available in limited quantities since January 1965, the English translation is available in limited quantities to technical libraries, government agencies, scientists, and nonprofit institutions concerned with air pollution. Those not qualifying for free copies can still obtain copies of the monthly journal, which contains technical articles on the effects and control of dusts, gases, vapors, and radioactive particles, with special emphasis placed on dealing with sources of community air pollution, at a subscription cost of \$24 a year. Separate issues can also be purchased. For information on the availability of this journal, address inquiries to the Clearing House for Federal Scientific and Technical Information, U.S. Department of Commerce, Springfield, Va. 22151

## ES&T Staff and Advisory Board Named

Dr. James J. Morgan, associate professor of environmental health engineering at California Institute of Technology, joined the Caltech faculty in 1965. He will edit the journal while continuing his duties as a faculty member.

Dr. Morgan received his B.C.E. in 1954 from Manhattan College, M.S.E. in 1956 from the University of Michigan, A.M. in 1962, and Ph.D. in 1964 from Harvard University. Both last year and in 1964 he chaired sessions at the Gordon Research Conferences and symposiums of the ACS Division of Water, Air, and Waste Chemistry. In 1965 he served as a member of the American Society for Engineering Education's Environmental Engineering and Science Committee, a member of the American Water Works Association's Task Group on Phosphates in Water, and chairman of AWWA's Research Committee on Iron and Manganese.

From 1956 to 1960 he was an instructor in sanitary engineering at the University of Illinois. In 1960-61 he held a Danforth Foundation Teacher Study Grant at Harvard and in 1961-63 continued his studies under a U.S. Public Health Service predoctoral fellowship. Dr. Morgan was appointed associate professor of water chemistry and research associate professor of civil engineering at the University of Florida in 1963. In 1964, Dr. Morgan served as a member of the National Institutes of Health's Environmental Sciences and Engineering Study Section.

He was awarded the Robert Ridgeway Prize of the American Society of Civil Engineers' New York Section in 1954, a Certificate of Merit from the ACS Division of Water, Air, and Waste Chemistry in 1962, and AWWA's Water Purification Division Award in 1963. Dr. Morgan is a member of ACS, AWWA, American Society for Limnology and Oceanography, American Society of Civil Engineers, American Association for the Advancement of Science, Sigma Xi, and Chi Epsilon.

Dr. Melvin J. Josephs, managing editor of ES&T, came to the new publication from *Chemical and Engineering News* where he had been associate editor in charge of the feature program. He received his B.Sc. (1950), M.Sc. (1952), and Ph.D. (1954) in plant physiology from Rutgers University. Dr. Josephs joined the agricultural chemists research group at Dow Chemical in 1954 where he worked in the herbicide section and developed techniques and pro-

grams for screening materials for the control of algae and aquatic weeds. In September of 1960 he joined the staff of C&EN as assistant editor in the Washington office and transferred to C&EN's New York news bureau in February 1961. In June of that year he opened C&EN's news bureau in Philadelphia where he remained until September 1963 when he returned to Washington to take over the feature program. He was named associate editor for C&EN in February 1964. Dr. Josephs is a member of ACS, Sigma Xi, and Phi Beta Kappa.

Katherine Biggs, manager, manuscript reviewing, has added ES&T to her already full schedule as manager of manuscript reviewing for five other ACS publications. A graduate of American University, College of Liberal Arts, Miss Biggs worked as a research associate in the National Bureau of Standards' Engine Fuels Section on a research project sponsored first by the Coordinating Research Council and later by the American Society for Testing and Materials. She joined the ACS Publications staff in 1949 as editorial assistant for *IE&C* and *Analytical Chemistry* and was promoted to assistant editor in 1951, then to associate editor in 1956. On the staff of the *Journal of Agricultural and Food Chemistry* from its start in 1953, Miss Biggs was appointed manager, manuscript reviewing, in 1965, having served in a similar capacity with the three *Industrial and Engineering Quarterly*s and the *Journal of Chemical and Engineering Data* since 1962.

Ruth Reynard, manager, manuscript editing, has taken on the extra responsibilities of manuscript editing for ES&T, a position she already holds for the three *Industrial and Engineering Quarterly*s and the *Journal of Chemical and Engineering Data* (since 1962), the *Journal of Agricultural and Food Chemistry* (since 1964), and the *Journal of Chemical Documentation* (since 1966). Miss Reynard received her B.A. in chemistry from the University of Mississippi in 1944. During the period 1944-46 she served in the WAVES (USN) as a pharmacist mate 2/c. Miss Reynard worked as a serologist for the U.S. Public Health Service from 1946-48, then for the New Orleans public health laboratories from 1948-49. In 1949 she went to Guatemala for the Pan American Sanitary Bureau (now Pan American Health



Dr. J. J. Morgan



Dr. M. J. Josephs



Katherine Biggs



Ruth Reynard



C. C. Sayre

Organization) as a serologist in a laboratory testing and technician training program. Miss Reynard then went to Los Angeles in 1952 where she was involved with a cancer research project under a University of Southern California grant. In 1953-56 she worked in the hygienic laboratory of the Arkansas Board of Health in Little Rock, after which (1957) she joined the ACS Publications in Washington, D.C., as an editorial assistant.

Charlotte C. Sayre, associate editor, supervises the ES&T production operations at our Easton office. Miss Sayre's responsibilities and those of three colleagues embrace, to various extents, a variety of functions: copy editing, proofreading, revising, and dummyping and layout. The Easton office is charged with maintaining effective relations between, and cooperating with, both the Washington staff and the printer so that publication schedules may be met. Miss Sayre adds ES&T to her portfolio which includes *Chemical and Engineering News*, the *Journal of Agricultural and Food Chemistry*, *Analytical Chemistry*, *In-*



Dr. S. K. Friedlander



Dr. E. D. Goldberg



Dr. H. P. Gregor

*ustrial and Engineering Chemistry* monthly as well as the three quarterlies, and *Chemistry*. Miss Sayre received her A.B. in mathematics from Wilson College (Chambersburg, Pa.) in 1932 and, that same year, joined Mack Printing Co. She switched to ACS Publications in 1936. Since then she has contributed much and in many ways to the success of these publications, particularly by urging editors and authors alike to be specific, concrete, and definite.

#### ADVISORY BOARD

*Dr. Morgan has appointed 10 members to ES&T's advisory board. Drawn from the ranks of those active in the fields of environmental science and technology, these men, representing a wide variety of disciplines and interests, will lend the benefit of their expertise and experience to the continuing effort of the new publication to serve its readers in the most com-*

*petent fashion. Meeting formally once or twice a year and keeping in touch with the editor and his staff by mail and phone, the advisory board serves to advise the editor on content and subject matter and to assist, when requested, in solving problems that may arise. Members of the advisory board are normally appointed to a three-year term. However, to maintain continuity and to establish a rotating appointment system, only four members have been appointed to three-year terms, three to two-year terms, and three to one-year terms.*

#### Three-Year Terms

**Dr. S. K. Friedlander** is professor of chemical engineering and environmental health engineering at California Institute of Technology, a position he has held since 1964. He came to Caltech from Johns Hopkins where he had been assistant professor of chemical engineering (1957-59), associate professor of chemical engineering (1959-62), acting chairman of the department of chemical engineering (1959-60), chairman of the biomedical engineering committee (1962), and professor of chemical engineering (1962-64). He received his B.S. in chemical engineering from Columbia University in 1949, his M.S. from MIT in 1951, and his Ph.D. from the University of Illinois in 1954.

Dr. Friedlander's research interests lie primarily in the fields of diffusion, interfacial transfer, and aerosol physics, particularly as related to problems of public health and medicine. His professional concern for matters of public health and medicine began during his residence as a research fellow at the Harvard School of Public Health in 1950-51.

He has published widely in applied physical chemistry, including condensation and fog formation, aerosol behavior, diffusion and chemical reaction, and the augmentation and retardation of interfacial mass transfer. Such work has application to air pollution, chemical processing, and physiology. Dr. Friedlander is a recipient of the Colburn Award (1959) given by the American Institute of Chemical Engineers. He has been a member of the environmental

sciences and engineering study section of the Public Health Service since 1965. He is a member of ACS, Sigma Xi, Tau Beta Pi, and Phi Lambda Upsilon.

**Dr. Edward D. Goldberg**, professor of chemistry, University of California, San Diego, received his B.S. from the University of California, Berkeley, in 1942, and his Ph.D. in chemistry from the University of Chicago in 1949. He spent four years in the Navy during World War II and joined the faculty of the University of California, San Diego, in 1949, as assistant professor of chemistry in the department of earth sciences. In 1961 he became a full professor. Dr. Goldberg served as the first provost of UCSD's Revelle College from February 1965 to July 1966.

Dr. Goldberg's major areas of scientific interest are the geochemistry of marine waters and sediments and the application of radioactive dating techniques to problems in the major sedimentary cycle. His current research programs include a study of the escape of helium from the earth's atmosphere, the potassium-argon dating of marine sediments, the use of glaciers in studying recent geological events at the earth's surface, fluorine geochemistry, and the input of man-made materials into the marine environment.

The author of more than 70 scientific articles, Dr. Goldberg has served as coeditor of a technical series in oceanography, "The Sea: Ideas and Observations," and as coeditor of the volume, "Earth Sciences and Meteoritics." He is an editor of two journals, *Earth and Planetary Science Letters* and *Journal of Marine Research*. He was elected vice-president of the Section of Volcanology in the American Geophysical Union in 1961.

**Dr. Harry P. Gregor**, professor of physical chemistry at Polytechnic Institute of Brooklyn, earned his B.A. (1939) and Ph.D. (1945, major—physical chemistry, minor—physiological chemistry) at the University of Minnesota. Following a year of industrial experience in the water-treatment industry, Dr. Gregor joined the faculty of the department of chemistry of Polytechnic Institute of Brooklyn.

Dr. Gregor's research interests have been in colloid and electrochemistry with particular emphasis on the study of high-polymeric materials. During his doctoral dis-





Dr. A. P. Altshuller



Dr. J. N. Pitts, Jr.



Dr. A. F. Gaudy, Jr.

sertation under the guidance of K. Sollner, he prepared the first ion exchange membranes of high permeability and selectivity, and has continued his interest in ion exchange phenomena. Dr. Gregor has prepared new ion exchange resin and membrane systems and has studied their basic properties. He has also collaborated in several investigations of the application of these systems to problems of separation and purification. He has published more than 100 papers in these and allied fields of interest.

Dr. Gregor's interests in environmental science and technology have led him to an active role as an advisor to many private and government agencies in the field of water purification and desalination. He was a "core" participant in writing the National Academy of Sciences-National Research Council "Woods Hole" report on desalination. He is a member of ACS.

**Dr. James N. Pitts, Jr.**, is professor of chemistry, University of California, Riverside, a position to which he was appointed in 1959. From 1961-63 he served as chairman of the department of chemistry. Also, he is a member of the Advisory Council for the Army Chemical Corps, the Study Section of Environmental Sciences and Engineering of the Public Health Service, and the committee on textile functioning finishing of the NAS-NRC Advisory Board on Military Personnel Supplies.

He received his B.S. (1945) and his Ph.D. in physical chemistry (1949) from the University of California, Los Angeles. Dr. Pitts worked as a research assistant (1942-45) for division 10, National Defense Research Committee, OSRD, and as research associate, special projects division, U.S. Army (1945-46). Then he was appointed instructor and assistant professor of chemistry at Northwestern University where he remained from 1949-54. From Northwestern he went to the University of California, Riverside, where from 1954-59 he was associate professor of chemistry.

Dr. Pitts is author or coauthor of more than 55 publications on photochemistry, air pollution, and related subjects. He is coeditor with W. A. Noyes, Jr., and G. S. Hammond of "Advances in Photochemistry," volumes I, II, III, and IV (Wiley-Interscience). Also, he is coauthor with J. C. Calvert of "Photochemistry" (John Wiley and Sons, 1966). He serves as coeditor with Dr. R. L. Metcalf on "Advances in Environmental Sciences and Technology" and a series of monographs and texts on "Environmental Sciences and Technology," published by Wiley-Interscience. In addition, Dr. Pitts has been the recipient of many grants and fellowships among which are grants by AEC (division of air pollution), Public Health Service, NSF-NRC, Air Force Research and Development Laboratory, and ACS for research in photochemistry and air pollution. He is a member of ACS, APCA, Faraday Society, Sigma Xi, Alpha Chi Sigma, Phi Lambda Upsilon, Phi Beta Kappa, and the American Physical Society.

## Two-Year Terms

**Dr. A. P. Altshuller** is chief of the Chemical Research and Development Section, Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Public Health Service at the Robert A. Taft Sanitary Engineering Center in Cincinnati, Ohio. He received his B.S. at the University of Chicago in 1948 and his M.S. (1950) and Ph.D. (1951) from the University of Cincinnati.

From 1951 to 1955 he was an aeronautical research scientist engaged in fuels research at what is now the Lewis Research Center of NASA. Since 1955 Dr. Altshuller has held various research assignments in the air pollution program at the Taft Center. He was appointed to his present position in 1961. He has published about 100 papers related to spectrophotometric analysis, gas chromatography, coulometric analysis, infrared spectrophotometry, photochemistry and kinetics, solution thermodynamics and statistical thermodynamics, thermochemistry, and various aspects of atmospheric chemistry. He is the chairman of the ACS Committee on Air Pollution, a member of the ASTM Committee on Air Pollution, and a member of APCA.

**Dr. A. F. Gaudy, Jr.**, is professor and acting head of Oklahoma State University's school of civil engineering. He has served as director of the Center for Water Research in Engineering (since 1965) and as chairman of the bioengineering and water resources program of the school of civil engineering (since 1964).

Dr. Gaudy received his B.S. in civil engineering (1951) from the University of Massachusetts, his M.S. in sanitary engineering (1953) from Massachusetts Institute of Technology, and Ph.D. in sanitary engineering (1959) from the University of Illinois.

Starting with Project Bluejay, Thule, Greenland, in 1951, Dr. Gaudy has had a wide variety of practical field and laboratory experience. After obtaining his Ph.D., Dr. Gaudy was appointed assistant professor of sanitary engineering at the University of Illinois (1959-61). From Illinois he went to Oklahoma State University where he was appointed associate professor (1961-63) and professor (1963) of civil engineering.

Dr. Gaudy is a consultant on industrial waste abatement problems that require a research approach. He serves also as a research consultant to NIH. And he has served, among many other jobs, as chairman of the industrial wastes conference program committee of the Oklahoma Water Pollution Control Association (1962-65), and as a member of the Oklahoma Water Resources Research Institute Advisory Board (1965 to present). He is author or coauthor of about 60 publications on a wide variety of subjects in environmental science and technology and he is a member of many professional and honorary societies including ACS, American Society of Civil Engineers, American Society for Microbiology, Water Pollution Control Federation, Ameri-



can Water Works Association, AAAS, American Public Health Association, and Sigma Xi.

**Dr. G. Fred Lee** is professor of water chemistry and director of the water chemistry program at the University of Wisconsin, Madison. He has published more than 30 papers in the field of the chemistry of natural waters, water and waste water treatment, and water pollution control. Dr. Lee is chairman of the special publications committee of the ACS Division of Water, Air, and Waste Chemistry and as such was a prime mover in the establishment of ES&T.

Dr. Lee received his B.S. in 1955 from San Jose State College (California), his M.S. in public health in 1957 from the University of North Carolina, and his Ph.D. in 1960 from Harvard University. From 1960-61 he was assistant professor of water chemistry at the University of Pittsburgh (Pennsylvania) before moving to the University of Wisconsin.

He is a member of the AWWA task group on nutrients in water, a member of the research committee on iron and manganese, and a member of the calcium and magnesium subcommittee of the Joint Committee for Uniform Method of Water Examination. Among his many professional and honorary societies are ACS, AWWA, Pollution Control Federation, American Society of Limnology and Oceanography, AAAS, American Geochemical Society, American Ecological Society, Sigma Xi, and Delta Omega.

#### One-Year Terms

**Dr. William L. Faith**, a consulting chemical engineer, has been involved in the field of environmental pollution for many years. He is currently a member (and past president) of the American Pollution Control Association, the sanitary engineering and occupational health study section of the U.S. Public Health Service, and the board of trustees of the American Sanitary Engineering Intersociety Board, Inc.

He received his B.S. from the University of Maryland (1928), his M.S. (1929) and Ph.D. (1932) in chemical engineering from the University of Illinois. He was a research chemist with National Aluminate Corp. (Chicago) in 1933, later joining the faculty of Kansas State College as assistant professor of chemical engineering, a post he held until 1936. He was appointed full professor in 1936 and served as department head until 1942. Dr. Faith then left to accept a position as professor and head of the department of chemical engineering at the University of Iowa where he remained until 1944.

During the war years he also served as a consultant to the chemical industry branch of the War Production Board's office of product research and development, was later made assistant director (1944), and then deputy director (1944-45). During the years 1944-45 he also served as visiting lecturer at Catholic University (Washington, D.C.), moving to Corn Products Refining Co. where he was director of de-

velopment engineering for the company's chemical division (1945-48) and later director of engineering (1948-54). Dr. Faith then joined the Air Pollution Foundation (San Marino, Calif.), where he served from 1954-57 as chief engineer, then from 1957-65 as managing director. He has served on the Los Angeles County Air Pollution Control Board since 1956.

**Dr. T. E. Larson**, assistant chief (since 1956) of the Illinois State Water Survey and head of its chemistry section (since 1946), received his B.S. in chemical engineering (1932) and Ph.D. in sanitary chemistry (1937) from the University of Illinois. Dr. Larson, who is also professor of sanitary engineering (since 1962) at the University of Illinois, is a licensed professional engineer in Illinois, and cooperates with the department of civil engineering at the University of Illinois in its instructional and research programs.

He joined the Illinois State Water Survey as assistant chemist in 1932 and was advanced to chemist in 1937. Dr. Larson has been active in many ACS programs and has served as chairman (1954), vice-chairman (1947 and 1953), and secretary-treasurer (1948-1952) of the Division of Water, Air, and Waste Chemistry. Among his many other activities he has also served as the ACS representative on the Public Health Service Drinking Water Standards Committee (1961). Dr. Larson has written more than 50 publications on such a wide variety of subjects as corrosion, water chemistry, analytical methods, and water treatment. He is a member of ACS, AWWA, AAAS, and NACE.

**Dr. Werner Stumm**, Gordon McKay Professor of Applied Chemistry at Harvard University since 1965, joined the Harvard faculty in 1956 as assistant professor of sanitary chemistry in Harvard's division of engineering and applied physics. In the years 1952-56 he served as a research associate at the Swiss Federal Institute of Technology, a position he took immediately after obtaining his Ph.D. in chemistry from the University of Zurich (Switzerland). Dr. Stumm's varied interests and broad experience in the field of environmental science and technology are focused on the chemistry of natural waters. The author of more than 50 scientific papers, most of his recent research work has concerned the properties of solid-solution interfaces with special emphasis on evaluating both the necessary chemical factors and the significance and role of the double layer in corrosion and coagulation phenomena. These investigations have led Dr. Stumm and others in the field to reappraise the mechanism of coagulation effected by hydrolyzed metal ions. Dr. Stumm is a member of ACS, chairman of the corrosion research committee of the American Water Works Association, and a member of the American Society of Civil Engineers. He has served as a research consultant to NIH on environmental science and engineering.



Dr. G. Fred Lee



Dr. T. E. Larson



Dr. Werner Stumm



Dr. W. L. Faith

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\*POLLUTION AND MARINE BIOLOGY by T. A. Olson and F. J. Burgess. Due April 1967.

PRINCIPLES AND APPLICATIONS OF WATER CHEMISTRY edited by S. D. Faust and J. V. Hunter. 1967. In press.

PRINCIPLES AND APPLICATIONS IN AQUATIC MICROBIOLOGY by H. Heukelekian and N. C. Dondero. 1964. 452 pages. \$10.00.

PRINCIPLES OF GEOCHEMISTRY, Third Edition, by B. Mason. 1966. 329 pages. \$9.95.

WATER AND WASTEWATER ENGINEERING by G. M. Fair, J. C. Geyer and D. A. Okun. Volume 1: Water Supply and Wastewater Removal. 1966. 516 pages. \$13.50. Volume 2: In preparation.

SEEPAGE, DRAINAGE AND FLOW NETS by H. R. Cedergren. 1966. Approx. 480 pages. Prob. \$13.50.

AQUEOUS WASTES: In Petroleum and Petrochemical Plants by M. R. Beychok. Due April, 1967. Approx. 376 pages. Prob. \$12.75.

\*Interscience Books

\*INDUSTRIAL HYGIENE AND TOXICOLOGY, Second Edition by F. A. Patty. Volume 1: General Principles. 1958. 858 pages. \$24.50. Volume 2: Toxicology. 1963. 1548 pages. \$40.00. Volume 3: In press.

\*THE ANALYTICAL TOXICOLOGY OF INORGANIC INDUSTRIAL POISONS by M. B. Jacobs. (Chemical Analysis Series, Volume 22) 1967. In press.

\*THE SEA: Ideas and Observations on Progress in the Study of the Seas edited by M. N. Hill. Volume 1: Physical Oceanography. 1962. 864 pages. \$27.50. Volume 2: The Composition of Sea Water; Comparative and Descriptive Oceanography. 1963. 554 pages. \$20.00. Volume 3: The Earth Beneath the Sea; History. 1963. 963 pages. \$28.00.

SEWAGE TREATMENT, Second Edition, by K. Imhoff and G. Fair. 1956. 388 pages. \$10.00.

UNIT OPERATIONS OF SANITARY ENGINEERING by L. G. Rich. 1961. 308 pages. \$9.95.

UNIT PROCESSES OF SANITARY ENGINEERING by L. G. Rich. 1963. 190 pages. \$7.95.

ENVIRONMENTAL SANITATION by J. A. Salvato, Jr. 1958. 660 pages. \$14.95.

CONSERVATION OF NATURAL RESOURCES, Third Edition, by G. H. Smith. 1965. 533 pages. \$9.95.

SALT WATER PURIFICATION by K. S. Spiegler. 1962. 167 pages. \$7.95.

GLOBAL IMPACTS OF APPLIED MICROBIOLOGY edited by M. P. Starr. 1965. 572 pages. \$15.00.

GROUND WATER HYDROLOGY by D. K. Todd. 1959. 336 pages. \$10.95.

\*ANTARCTIC GEOLOGY Proceedings of the SCAR International Symposium, edited by J. R. Adie. 1965. 758 pages. \$32.50.

SEWERAGE AND SEWAGE TREATMENT, Eighth Edition, by H. E. Babbitt. 1958. 790 pages. \$12.50.

GEOHYDROLOGY by R. J. M. DeWiest. 1965. 366 pages. \$11.50.

\*GENERAL OCEANOGRAPHY by G. Dietrich. 1963. 588 pages. \$21.00.

ELEMENTS OF WATER SUPPLY AND WASTE-WATER DISPOSAL by G. M. Fair and J. C. Geyer. 1958. 615 pages. \$10.95.

AIR POLLUTION CONTROL by W. L. Faith. 1959. 259 pages. \$8.95.

\*MICROBIOLOGY OF THE ATMOSPHERE by P. H. Gregory. (A Plant Science Monograph) 1962. 252 pages. \$10.95.

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## Congress Looks at Pollution Control Technology

**Environmental Pollution—A Challenge to Science and Technology.** A summary report of the U.S. House of Representatives Subcommittee on Science, Research, and Development. Prepared by Richard A. Carpenter. 60 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1966. 20 cents

*Hearings before the Subcommittee on Science, Research, and Development of the Committee on Science and Astronautics, U.S. House of Representatives, 89th Cong., 2nd sess., Volumes I and II, July 20-1, 26-8, Aug. 3-4, 9-11, and Sept. 19, 1966. Available at most libraries or through interlibrary loan.*

"There is no need for detailed instrumental measurement or for emotional appeals of naturalists, we freely admit that we have a problem. Further definition of the problem, however, becomes a very difficult project involving natural and social sciences, economics, and governmental and private institutions. Making appropriate choices as we proceed will depend on much more knowledge than we now have." So states an early paragraph in a report of the Subcommittee on Science, Research, and Development to the U.S. House of Representatives Committee on Science and Astronautics.

Known popularly as the Daddario Committee (chairman Emilio Q. Daddario, D.-Conn.), the subcommittee sought to prepare a report that might help in defining the role of science and technology in pollution abatement. To achieve these goals the subcommittee members spent 11 days in July and August of last year hearing and reading testimony from 28 witnesses who represented Congressional committees, federal agencies, state and local governments, industry, universities, private research organizations, and citizen action groups.

Altogether the subcommittee made available 915 pages of transcripts of the hearings plus a 60-page report. Volume I of the hearings is largely a transcript of the exchange between the subcommittee members and the witnesses. Vol-

ume II is devoted to a presentation of a considerable body of information that includes responses by witnesses to questions submitted to them after the hearings proper, some prepared statements by witnesses, and a variety of material published at various times or presented at meetings. The report serves as a summary of the hearings in general, the first 36 pages devoted to a summary of the hearings per se, and the final 24 pages to a summary appendix.

The hearing transcripts show the give and take between the witnesses and the subcommittee members and have kind of an excitement about them as one gets involved in the ebb and flow of opinion, facts, attitudes, and prejudices.

### **Skillful summary**

The distillation of all these inputs, however, has been skillfully prepared and takes on an aura of immediacy and significance. The report, actually prepared by Richard A. Carpenter, senior specialist in science and technology of the science policy research division of the Library of Congress is, indeed, the "concise and objective analysis of the testimony" presented that the subcommittee claims. Lest anyone doubt it, this report, if for no other reason than its candor, competence, and cohesiveness is—and will continue to be for many years—a critically important document in the pollution control field.

The subcommittee summarizes the hearings first by conveying the subcommittee's impressions:

- There is no place left in the world for waste.
- Manmade disruptions have increased to the point where mistakes or unknown effects may be profound and irreversible.
- Conservation of resources means recycling because none of our natural resources is in so ample a supply that it can any longer be considered inexhaustible.
- There is no time left for adaptation because the environmental effects are huge.
- There is a need for additional sci-

ence and technology because not enough attention has been devoted to these two sectors.

The subcommittee recognizes that technology is available to accomplish many of the technical goals that we might wish to achieve. But, the subcommittee cautions, technology cannot always achieve the desired technical goals at a cost that fits the value judgments of the society it seeks to serve.

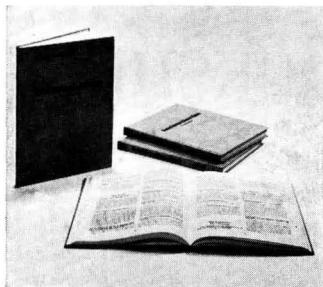
The subcommittee, in a fanciful mood, observed that pollution is often well understood—until a definition is requested. The simple term "too much" is useful, the report states. But probably the most significant concept may be the one which conceives environmental pollution as waste management gone wrong.

The subcommittee settled on this particular concept because, as the report says, wastes will be with us always. Therefore, the key to achieving and maintaining satisfactory quality of our surroundings is the control of wastes at all times—until they are recycled for further use of safely transferred to long-term storage. "It is when we do not know where wastes are, or do not take the trouble to confine and control them, that unwanted contamination occurs."

### **Middle ground**

The subcommittee notes in the report the need for an early warning system to notify society of unwanted consequences resulting from the risks it takes with natural resources. The committee, further, steers a rather precise course between an unrealistic zero point of contamination and the opposite, a "public be damned" attitude.

Firm criteria and standards for environmental quality are necessary before a sound planning and action program can occur. To achieve this goal there is a need for rapid expansion of research and development, which must come from the private sector rather than the federal laboratories simply because the federal laboratories cannot expand fast enough. Nor are the Federal Government's scientific activities in the field of pollution sufficiently coordinated to be susceptible



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to a systems analysis or broad management operations.

Large-scale demonstrations of new and improved abatement methods are necessary to establish realistic and practically applicable efficiency and cost data. This kind of demonstration requires government underwriting or risk sharing. In this regard, the problems of pollution are markedly different from the problems of the military space programs, the report notes. Because the Federal Government is not the major customer for the products and processes resulting from R&D on pollution, something must be done to stimulate the industrial or other private sectors to develop abatement standards. Federal research support should be used to develop methods, but abatement technology should be in the control of normal commercial enterprise, a statement which seemingly puts the Daddario Committee at odds with Sen. Russell Long (D.-La.).

### Reasoned approach

All in all, the report is a sober, reasoned, in-depth approach to the general problems of pollution, the general level of science and technology available to solve these problems, and the needs and motivations outside the social, scientific, and political framework necessary to accomplish a wholly effective pollution control system.

There may be some doubt that this report and its associated volumes on the hearings covered the entire pollution problem adequately. But such coverage was never attempted. The subcommittee members were not so presumptuous as to think that they could cover such a vast problem in a short time or with ease.

What the subcommittee hoped to do and, indeed, what it appears to have achieved, is to provide a balanced and useful insight into the technological adequacy of the nation, in all its operating areas, to accomplish an effective pollution control program. Without going the route of the witch hunters but, on the other hand, avoiding the timidity of the fence-straddler, the subcommittee pointed fingers and patted backs as appropriate.

This document, not only from the point of view of pollution abatement but also because it sets a stunning example of an enlightened and competent Congressional committee at work, should serve as a masterful example for other investigating groups. The com-

mittee carefully listened to representatives of all sectors having an expressed interest in pollution abatement on a national scale, and the report is a competent reflection of a balanced and careful inquiry.

**A Directory of Information Resources in the United States: Water.** National Referral Center for Science and Technology. v + 248 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1966. \$1.50 paper.

The directory is a comprehensive listing and description of the many organizations and institutions in the U.S. doing research or collecting data on water and water-related subjects. The focus is on fresh water, and thus the directory largely excludes the field of oceanography. Nor does the directory include commercial or profit-making organizations involved in water research. The directory is, nonetheless, a valuable guide because it describes each listed organization's areas of interest, its publications, holdings, and the services it provides. In addition, the directory contains an organization index and a subject index, both cross referenced.

**Environmental Biology.** Compiled and edited by Philip A. Altman and Dorothy S. Dittmer. xxi + 694 pages. Federation of American Societies for Experimental Biology, Bethesda, Md. 20014. 1966. \$15.00 hard cover.

**The Economics of Air Pollution.** Edited by Harold Wolozin. 318 pages. W. W. Norton & Co., Inc., New York, N.Y. 10003. 1966. \$2.95 paper.

**Particles in the Atmosphere and Space.** Richard D. Cadle. viii + 226 pages. Reinhold Publishing Corp., New York, N.Y. 10022. 1966. \$10.00 hard cover.

**Organic Pesticides in the Environment.** Edited by Robert F. Gould. x + 309 pages. American Chemical Society Publications, Washington, D.C. 20036. 1966. \$8.50 hard cover.

**Scientific Aspects of Pest Control.** A symposium. xi + 470 pages. Publication 1402, National Academy of Sciences—National Research Council, Washington, D.C. 20418. 1966. \$5.00 paper.

# MEETING GUIDE

## **February 6-7 American Chemical Society, Middle Atlantic Region**

Second Middle Atlantic Regional Meeting of the ACS

New York Hilton Hotel, New York, N.Y.

Among many technical papers and symposiums are two of special interest to workers in the field of environmental science and technology.

Symposium on Air Pollution Abatement. Invited papers only. This session will discuss management of the air resource as viewed by New York City, the control of industrial stack emissions, and automotive exhaust control.

Symposium on Economics of Air Pollution Control. Invited papers only. This session will focus on the economic problems—and suggested solutions—of effective air pollution control as seen by the Federal Government, industry, and public utilities.

## **February 6-9 American Society of Civil Engineers**

Engineering for the Megalopolis

Statler-Hilton Hotel, Dallas, Tex.

The conference will include many technical papers on pollution matters, such as advances in air pollution control, mathematical model of pollutant distribution in natural streams, water resources projects and recreational areas, energy and air pollution, local, state, and regional approaches to air pollution control, and waste assimilation capacity as a tool in water resources management.

## **February 7-8 Ninth Sanitary Engineering Conference**

Instrumentation, control, and automation for water supply and waste-water treatment plants

University of Illinois, Urbana, Ill.

The conference will consider the pros and cons of instrumentation, controls, automation, and monitoring devices for operation and control of water and waste-water systems. Included will be papers on present and future uses and design features for instruments and computers needed to provide physical and chemical measurements for research, plant operations, and enforcement purposes.

## **March 13-17 National Association of Corrosion Engineers**

23rd Conference and 1967 Corrosion Show

Biltmore Hotel, Los Angeles, Calif.

Directed to the prevention, detection, and control of corrosion, the conference has scheduled symposiums on corrosion problems related to waste water and sewage, metals in concrete, high temperatures, domestic water, sea water, high purity water, military equipment, and high-voltage direct-current transmission.

## **March 21 Metropolitan Engineers Council on Air Resources, American Society of Mechanical Engineers (Incinerator Committee)**

Incineration of Solid Wastes

Sheraton-Atlantic Hotel, New York, N.Y.

The one-day meeting will include discussions of the composition and combustion of refuse, a new incinerator at Munich (West Germany), how refuse is used to fire a steam generator, the economics of solid waste incineration, industrial incinerators, and control equipment for incinerators. Typical of ME-CAR's meetings, the sessions will end with an author summary panel with discussion from the audience invited. Attendance is by pre-registration only. Address Robert A. Fox, P.O. Box 607, Grand Central Post Office, New York, N.Y. 10017.

## **April 9-14 American Chemical Society 153rd National Meeting**

Miami, Fla.

In addition to the many papers at the 153rd National Meeting that will touch on matters of interest to those involved in environmental studies, there are two special symposiums dealing exclusively with such matters.

Symposium on Trace Inorganics in Water. Invited papers only. Divided into three major sessions, the symposium will include fundamentals, applied, and analytical considerations involved in the study and understanding of trace inorganics in water.

Symposium on Water Chemistry (Joint with Division of Chemical Education)

Invited papers only. The theme of this symposium is the role of chemists in the study of natural waters, water and waste-water treatment, and water pollution control. Areas of water chemistry included in the symposium are analytical methods, municipal and industrial water treatment, water pollution control, ground water, lakes, rivers, and marine waters.

Three additional Division of Water, Air, and Waste Chemistry programs also bear on problems of environmental research and development:

Scientific Information Resources for the Water Researcher (Joint with Division of Chemical Literature)

General Papers, Water.  
General Papers, Air.

## **April 10-12 Institute of Environmental Sciences 1967 Technical Meeting and Equipment Exposition**

Shoreham Hotel, Washington, D. C.

The meeting is divided into a technical section and a tutorial section. The technical section will include sessions on environmental management and equipment, simulation instrumentation, space, earth, and marine environment, and the specialty areas of dynamics, electromagnetic interference, and thermo-environment associated with high speed flight. The tutorial section will be directed to the new interests of marine and space environments as well as simulation and instrumentation techniques.

## **May 2-5 New York Academy of Sciences**

Biological Effects of Pesticides

Waldorf-Astoria Hotel, New York, N.Y.

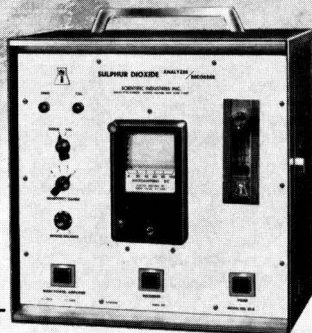
The conference is directed especially to members of the scientific community who are in a position to contribute to the further sophistication of research on health and related aspects of pesticides. Conference participants will include world authorities on toxicology, metabolism, mode of action, and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



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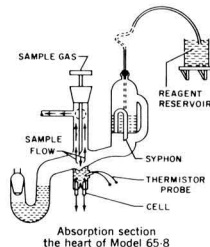
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### MEETING GUIDE continued

**May 15-17**

**U.S. Atomic Energy Commission,  
Ecological Society of America, Uni-  
versity of Michigan**

Second National Symposium on Radioecology

Horace H. Rackham Lecture Hall,  
University of Michigan, Ann Arbor,  
Mich.

Subtitled Nuclear Energy in Man's Environment: Past, Present, and Future Problems, the symposium is designed to acquaint ecologists with the problems arising from the release of radiation to the environment—and how such problems have been treated in the past, so that future radiation hazards may be dealt with adequately. The sponsors are soliciting papers. Title, author, and a 200-word abstract of proposed papers should be directed by Feb. 1 as follows: **Nuclide Cycling**, Dr. E. J. Kuenzler, Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, N.C.; **Radiation Effects**, Dr. C. A. Tryon, Jr., Biological Sciences, University of Pittsburgh, Pittsburgh, Pa.

**June 11-16**

**National Research Council  
(Division of Biology and Agriculture)**

International Symposium on Eutrophication

University of Wisconsin, Madison, Wis.

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

**August 23-25**

**American Society of Civil Engineers  
(Sanitary Engineering Division)**

National Symposium on Estuarine Pollution

Stanford University, Stanford, Calif.

Designed to satisfy the needs of sanitary engineers and scientists concerned with the effects and control of pollution in estuaries, the symposium will cover recent studies on the effects of municipal, industrial, and agricultural pollutants on water quality and aquatic life, as well as the distribution of such pollutants by tidal action, wind, sunlight, temperature, and other physical, chemical, and biological factors. Also planned are discussions on forecasting techniques, model studies, and recent developments in water quality management. The sponsors are soliciting papers. Title, author, and a 200-300 word abstract of proposed papers should be sent by March 15 to Robert M. Kennedy, program chairman, Kennedy Engineers, 604 Mission St., San Francisco, Calif. 94105.

**ENVIRONMENTAL SCIENCE AND TECHNOLOGY** places special emphasis on reporting original chemical research, engineering developments, and technico-economic studies in fields of science directly related to man's environment. Contributed articles should be directed to scientists and engineers concerned with fundamental and applied aspects of water, air, and waste chemistry and other relevant fields. These may include, but are not to be restricted to engineering, biology, ecology, economics, soil sciences, atmospheric sciences, geological sciences, marine sciences, and medical sciences. Contributions may emphasize improved understanding of water, air, and wastes from the viewpoint of their roles in pollution and its control and may consider their relationship to industrial and social progress. Because a meaningful approach to the management of environmental quality involves more than scientific understanding, ES&T will devote serious attention to engineering, economic, legal, and other influences to give its readers an integrated view of this complex system.

The research pages of the journal are devoted to the publication of contributed and critically reviewed papers concerned with the fields of water, air, and waste chemistry, in particular, and with other scientific and technical fields, including the social sciences, which are relevant to the understanding and management of the quality of the air, water, and land environments. The journal attempts to serve the research interests of all scientists and engineers whose work falls within the broad field of environmental science and technology.

Contributed papers will, in general, describe results of original research. Review articles will be considered when they serve to provide new research approaches or stimulate further worthwhile research in a significant area.

In addition to full length articles, the journal will publish Communications. Communications may be letters describing preliminary results of immediate interest, or they may be significant comments on the work of others. The author of the work discussed will, ordinarily, be allowed to reply.

## AUTHOR'S GUIDE

This manuscript preparation guide is published to aid authors in writing, and editors and reviewers in expediting the review and publication of manuscripts in **ENVIRONMENTAL SCIENCE AND TECHNOLOGY**.

### *Abstracts*

An abstract which will appear at the beginning of the paper must accompany each manuscript. Authors' abstracts are frequently used directly for *Chemical Abstracts*. Use between 100 and 150 words to give purpose, methods or procedures, significant new results, and conclusions. Write for literature searchers as well as journal readers. No abstracts are used for Communications.

### *Short Summary*

The Short Summary is used on the contents page to bring to the attention of all ES&T readers the latest account of current research. These summaries should be from 50 to 100 words and should highlight what the article *says*, NOT what it is *about*; that is, they should summarize the *contents* of the article, not merely discuss the subject area. The purpose of the Short Summary is to help the interested reader who is not necessarily competent in the specialized field encompassed in the paper to extract the meaningful information in the paper, and to determine whether he should pursue the subject in greater detail.

### *Title*

Use specific and informative titles. They should be as brief as possible, consistent with the need for defining the subject of the paper. If trade names are used, give generic names in parentheses. Effective literature retrieval depends on the information conveyed by the title.

### *Authorship*

List the first name, middle initials, and last name of each author. Omit professional and official titles. Underline the

name of the senior author, to whom all correspondence will be sent. Give the complete mailing address where work was performed. If present address of author is different, include it in a footnote.

### *Text*

Consult a current issue for general style. Assume your readers to be capable professionals not necessarily expert in your particular field. Historical summaries are seldom warranted. However, documentation and summary material should be sufficient to establish an adequate background. Divide the article into sections, each with an appropriate heading, but do not oversectionalize. The text should have only enough divisions to make organization effective and comprehensible without destroying the continuity of the text. Keep all information pertinent to a particular section within that section. Avoid repetition. Do not use footnotes; include the information in the text.

*Introduction.* Discuss relationship of your work to previously published work, but do not repeat. If a recent article has summarized work on the subject, cite the summarizing article without repeating its individual citations. *Apparatus.* List devices only if of specialized nature. *Reagents.* List and describe preparation of special reagents only. *Procedure.* Omit details of procedures which are common knowledge to those in the field. Brief highlights of published procedures may be included, but details must be left to literature cited. Describe pertinent and critical factors involved in reactions so the method can be reproduced, but avoid excessive description. *Results and Discussion.* Be complete but concise. Avoid comparisons or contrasts which are not pertinent. Draw clearly all warranted inferences.

### *Tables, Graphs, and Illustrations*

Avoid tables and graphs which duplicate information. In general, graphs are preferable to tables, if precise data are not required. Lengthy data tables are usually not necessary. How-

ever, certain types of articles—for example, those where correlation methods are compared—do require more than the usual quantity of data. Furnish tables with appropriate titles, and number them consecutively. For details on how to prepare all such material see section on Copy Requirements.

#### Nomenclature

The nomenclature should correspond, as closely as possible, to the style of *Chemical Abstracts*. Do not define terms in the text unless there is a particular need.

Use consistent units of measure (preferably metric).

If nomenclature is specialized, include a "Nomenclature" section at the end of paper, giving definitions and dimensions for all terms. Write out names of Greek letters and special symbols in margin of manuscript at point of first use. Complete definition includes dimension of each term. If subscripts and superscripts are necessary, place them accurately. Avoid trivial names. Trade names should be capitalized and defined at point of first use. Identify typed letters and numbers which could be misinterpreted, for example, one and the letter "1," zero and the letter "O."

#### Formulas and Equations

Chemical formulas should correspond to the style of *Chemical Abstracts*. Chemical equations should be balanced and numbered consecutively along with mathematical equations. The mathematical portions of the paper should be as brief as possible, particularly where standard derivations and techniques are commonly available in standard works.

#### Safety

Authors are requested to call special attention—both in their manuscripts and in their correspondence with the editors—to safety considerations such as explosive tendencies, special precautionary handling procedures, and toxicity.

#### Acknowledgment

Include essential credits in an "Acknowledgment" section at the end of the text, but hold to an absolute minimum. Give meeting presentation data or other information regarding the work reported (for example, financial support) in a note following Literature Cited.

#### References

Literature references should be listed in alphabetic order by author, patentee, or equivalent. "Anonymous" is not acceptable for authorship. If the author is unknown, list the reference by company, agency, or journal source. Do not number references. Within the text, references should be cited as follows: one author (Saltzman, 1954); two authors (Burnet and Stanley, 1959); more than two authors (Burnet, Stanley, *et al.*, 1959). Do not list references as "in press" unless they have been formally accepted for publication. Give complete information, as in examples, using *Chemical Abstracts* abbreviations for titles of periodicals.

For a periodical reference to be considered complete, it must contain the author's(s') complete name(s), journal source, volume number, issue number (if any), the first and last page numbers of the article, and the year of issue. State if a reference is in a language other than English.

Give complete information when citing articles, books, patents, and the like, according to the following examples:

Altshuller, A. P., Division of Water, Air, and Waste Chemistry, 150th Meeting, ACS, Atlantic City, N.J., September 1965.

Burnet, F. M., Stanley, W. M., Eds., "The Viruses," Vol. 1, pp. 609–15, Academic Press, New York, 1959.

Chen, D. H. T., M.S. thesis, University of Rhode Island, Kingston, R.I., 1961.

Handbook of Colorimetric Chemical Analytical Methods, 5th ed., pp. 13–15, Tintometer Ltd., Salisbury, England (1959).

Luthy, R. V. (to California Research Corp.), U.S. Patent 2,855,444 (Oct. 7, 1958).

Pollard, N. D., FMC Corp., Baltimore, Md., private communication, 1962.

Saltzman, B. E., *Anal. Chem.* **26**, 1949–55 (1954).

Schmauch, L. J., Grubb, H. M., *Anal. Chem.* **26**, 308–11 (1954).

U. S. Department of Health, Education, and Welfare, Public Health Service, Cincinnati, Ohio, "Selected Methods for Measurement of Air Pollutants," 1965.

#### Copy Requirements

Three complete copies of the manuscript are required. They should be typed double- or triple-spaced on 8½- by 11-inch paper, with text, tables, and illustrations of a size that can be mailed to reviewers under one cover. Duplicated copies will be accepted only if very clear.

If pertinent references are unpublished, furnish copies of the work or sufficient information to enable reviewers to evaluate the manuscript.

Submit original drawings (or sharp glossy prints) of graphs and diagrams prepared on tracing cloth or plain paper. All lines, lettering, and numbering should be sharp and unbroken. If coordinate paper is used, use blue cross-hatch lines as no other color will "screen out." Typed lettering does not reproduce well; use black India ink and a lettering set for all letters, numbers, and symbols. On 8- × 10-inch copy, lettering should be at least 1/8 inch high and 0.017 inch thick—for example, with a Leroy lettering set, use template 120 C and pen No. 0. Lettering on copy of other sizes should be in proportion. Label ordinates and abscissas of graphs along the axes and outside the graph proper.

Type tables (double-spaced lines, wide margins) on separate pages. Furnish charts and graphs in a form that can be photographically reproduced with ease. Photographs should be as large as possible, preferably 8 × 10 inches. Supply glossy prints of photographs. Sharp contrasts are essential.

Number all illustrations consecutively using Arabic numerals in the order of reference in the text. Include a typed list of captions and legends for all illustrations on a separate page.

If drawings are mailed under separate cover, identify by name of author and title of manuscript. Advise editor if drawings or photographs should be returned to the authors.

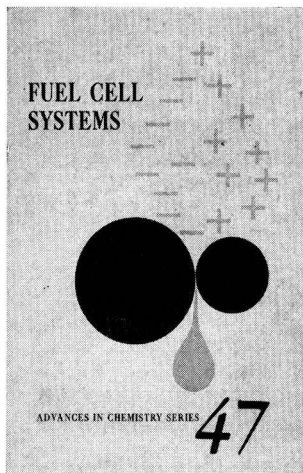
Prepare tables in consistent form, furnish each with an appropriate title, and number consecutively using Roman numerals in the order of reference in the text. Double space.

In case of doubt, please consult editors.

The manuscripts with a covering letter should be sent to:

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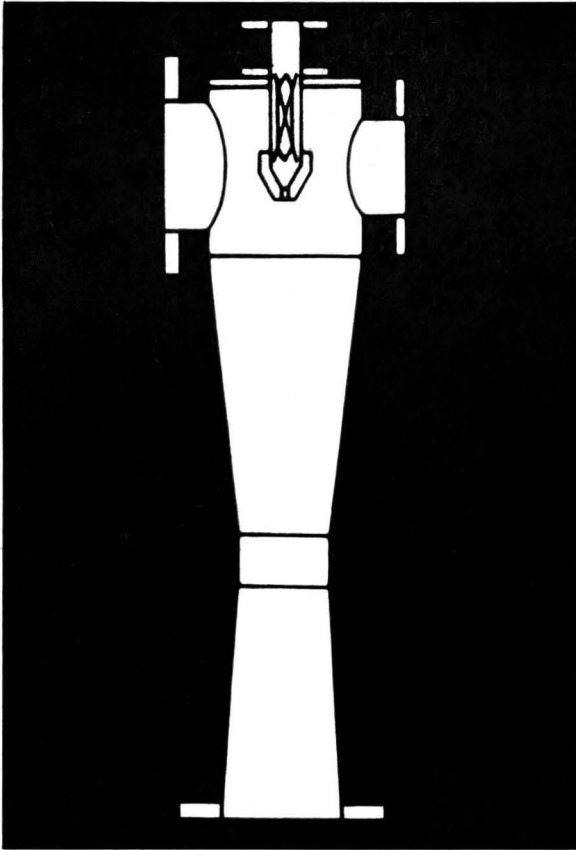
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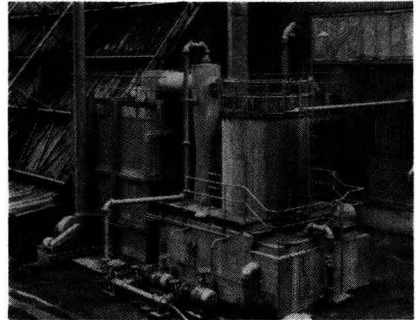


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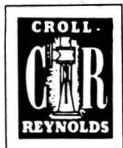
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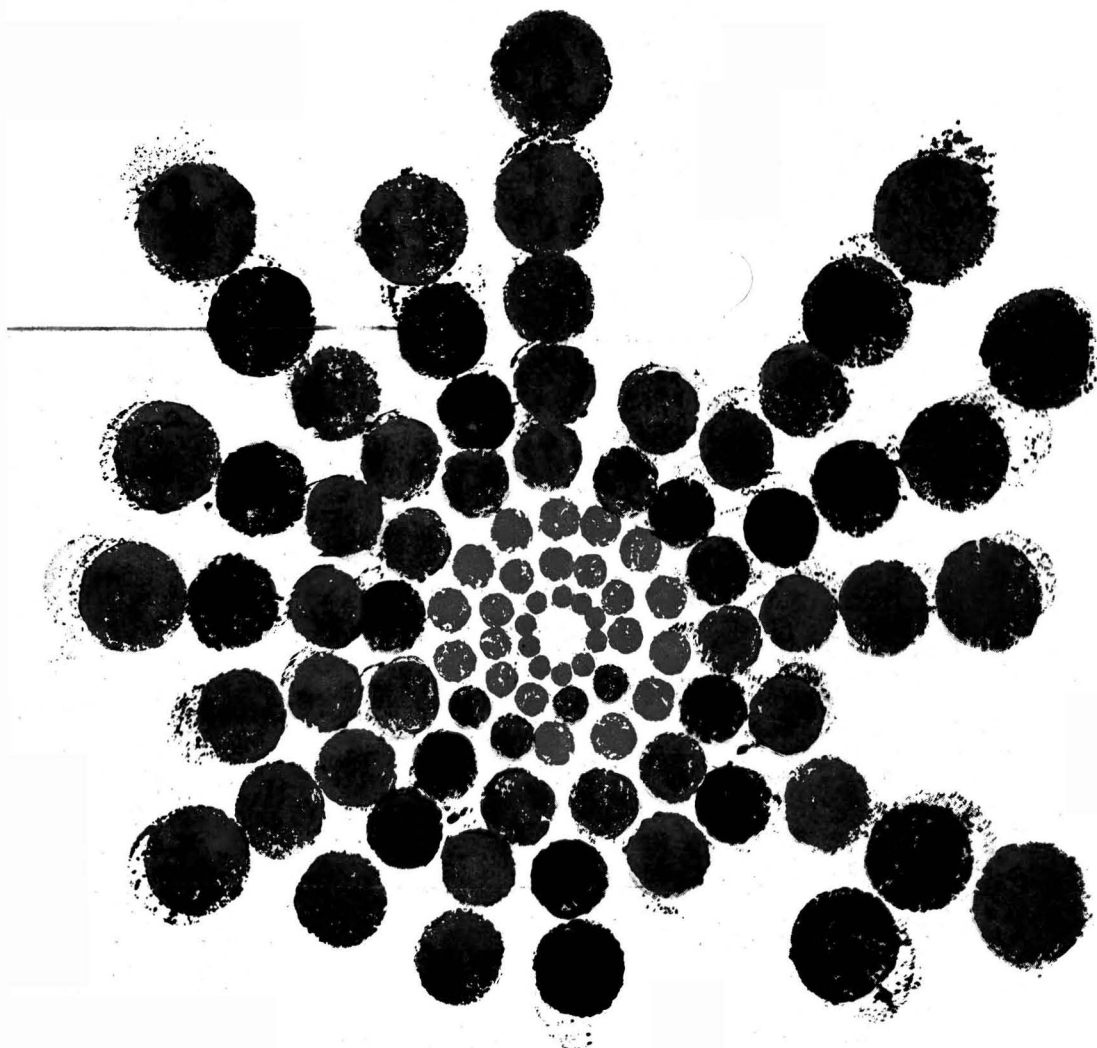
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As man has industrialized, potential problems due to pollution of air and water have increased. Industry and government officials have joined in efforts to solve mounting concerns.  UOP, respected for its technical achievements in the petroleum and chemical industries, has taken a broad position of leadership to alleviate these problems. We offer the widest selection of air correction equipment and systems, and provide a complete range of air pollution control services from consultation and source testing to equipment design and field start-up.  Our work in environmental engineering is not limited

to the control of pollutants in the atmosphere or recovery of valuable material in process streams. UOP also is active in water management—providing chemicals, equipment and services used in commercial water conditioning, including screens and filters used in food processing, mining, architectural applications and general water treatment.  Competent technical help in solving your air and water correction problems is available now. Environmental engineering is another example of UOP's contribution to technological progress. UOP, 30 Algonquin Rd., Des Plaines, Illinois 60016.

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