



# ENVIRONMENTAL Science & Technology

*Emphasizing*

*Water,*

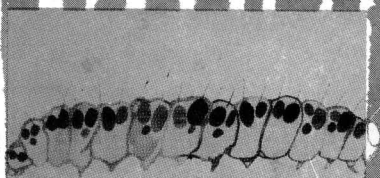
*Air, &*

*Waste*

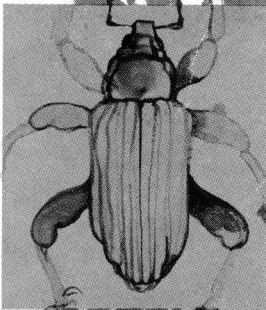
Chemistry

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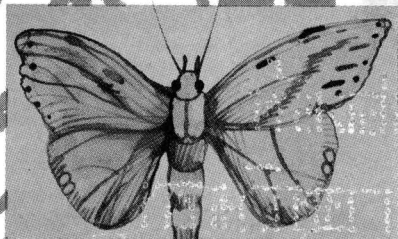
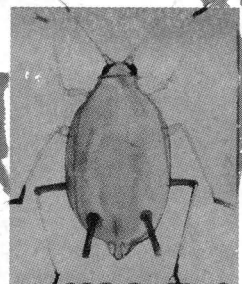
*Soybean*



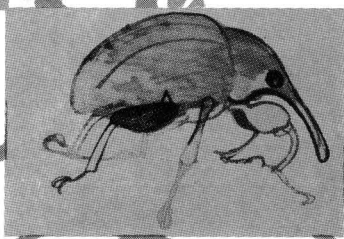
*Rice*



*Cotton*



*Tobacco*



Pesticides:  
20 years later 619

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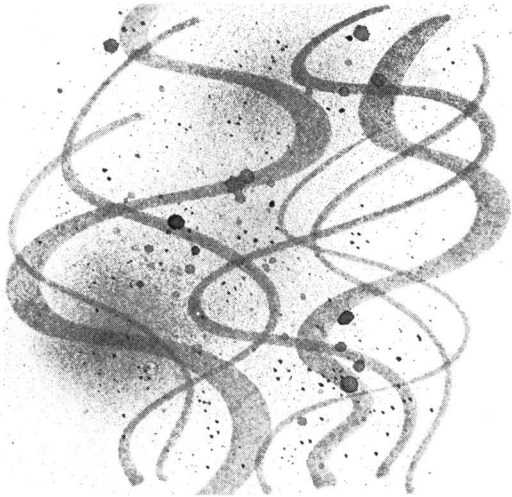
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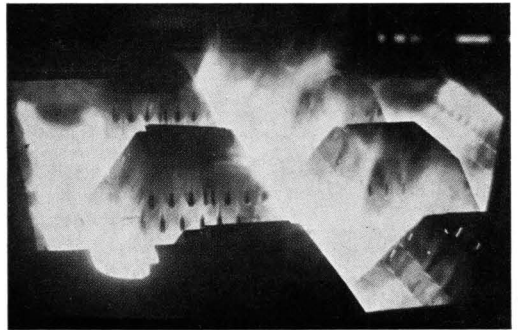
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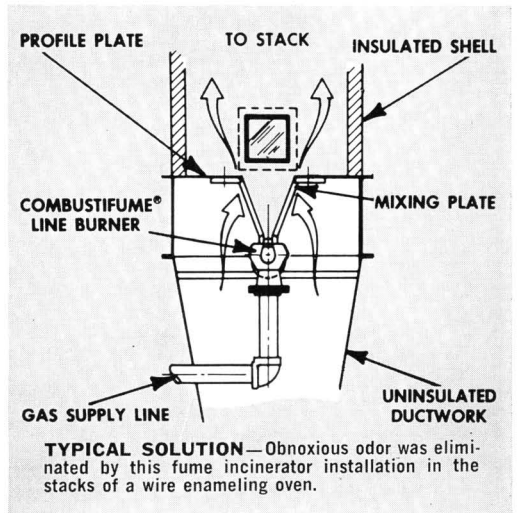
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July 1969

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# contents

## Current research

- Aerosol size spectrometry with a ring slit confuge** 641  
W. Stober and H. Flachsbar

The determination of particle size distribution, probably the most ambiguous of all basic experimental analyses in aerosol research, can be determined at high aerosol sampling rates using a modified confuge with a ring slit aerosol inlet. Sampling rates of one liter per minute or more for aerosol particles with diameters in the range of  $4 \times 10^{-4}$  to  $1.3 \times 10^{-6}$  cm. can be accommodated with size resolutions of better than 7%.

- Absolute calibration of a flame photometric detector to volatile sulfur compounds at sub-part-per-million levels** 652  
R. K. Stevens, A. E. O'Keefe, and G. C. Ortman

The flame photometric detector (FPD) has potential in a continuous air monitoring device for sulfur compounds—sulfur dioxide, hydrogen sulfide, methyl mercaptan, and carbon disulfide at the 0.001–10 p.p.m. concentration levels. An instrument using this detector would not need the constant daily attention required for current air monitoring instruments that are based on conductimetric, colorimetric, or coulometric principles. Permeation tubes were used to calibrate the FPD.

- Solubility of gypsum in aqueous electrolytes as affected by ion association and ionic strengths up to 0.15 M and at 25° C.** 656  
K. K. Tanji

The solubility of gypsum, possibly the principal salt causing salinity in natural waters of arid regions, can be predicted by means of a computer program. The computer predictions have significance in agriculture, hydrochemistry, and geochemistry. The computer program can be used to predict the solubility of gypsum in several aqueous electrolytes and in water, and the precipitation of gypsum in admixtures of salt solutions initially free of solid phase gypsum.

- Removal of orthophosphates from aqueous solutions with activated alumina** 661  
R. D. Neufeld and G. Thodos

Activated alumina is used for the essentially quantitative removal of phosphate nutrients from aqueous solutions. Columns from 1.97–26.0 cm. in height can be used with solutions containing from 10–120 mg. of phosphate per liter of solution. Initially, the removal is accompanied by an exchange with the nitrates present on the solid alumina, and followed by reformation of the phosphate deposited on the solid surface with phosphate in solution to effect further removal.

- Fractionation of bomb-produced rare-earth nuclides in the atmosphere** 667  
M. Thein, J. N. Beck, H. Johnson, W. W. Cooper, M. A. Reynolds, R. S. Clark, J. O. Baugh, and P. K. Kuroda

Global atmospheric fractionation of nuclear debris helps to explain the process of fallout from nuclear weapons tests. Rare earth radionuclides as well as Sr, Ba, Te, and I isotopes from the Chinese nuclear detonation (Dec. 24, 1967) were found in the rain collected at Fayetteville, Ark.

- Vapor density of dieldrin** 670  
W. F. Spencer and M. M. Cliath

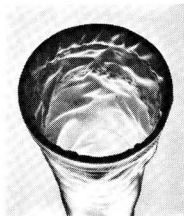
The vapor density of the pesticide dieldrin in soil samples containing the pesticide is 3–12 times larger than that predicted from published vapor pressure values. The vapor density of soil samples containing the pesticide at a concentration level of 100 p.p.m. is the same as that of neat dieldrin, but the vapor density of soil samples containing 10 p.p.m. dieldrin was reduced 80%. Water has no appreciable effect on vapor density or potential vaporization rate of dieldrin.

## Communication

- Apparatus for continuous solids-liquid separation** 674  
M. J. Ryan

Frequently, in the use of activated sludge for the degradation of human wastes into nonnoxious compounds, the continuous separation of solids from liquids is required. New apparatus avoids the use of rotary vacuum seals and can be used at suspended solids levels approaching 20 grams per liter. The units can be considered modular; several units can be connected in parallel.

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## **Nixon announces environmental quality council**

By executive order, President Richard Nixon created the Environmental Quality Council, a new cabinet-level advisory group which will be a focal point for this administration's efforts to protect all natural resources. At present, the eight member group consists of the President, Vice President, and Secretaries of the Departments of Agriculture; Commerce; Health, Education, and Welfare; Housing and Urban Development; Interior; and Transportation. Lee A. DuBridge, science advisor to the President, will serve as executive secretary to the council, whose structure, in some respects, parallels that of the National Security Council and the Urban Affairs Council. DuBridge says that immediate priority will be given to the harmful effects of prolonged use of DDT, methods of solid waste disposal, and air pollution. At the same time, the executive order created a 15 member Citizens' Advisory Committee on Environmental Quality. Under the chairmanship of the noted conservationist, Laurance S. Rockefeller, this committee stems from the activities of the Council on Recreation and Natural Beauty which gave us "From Sea to Shining Sea, A Report on the American Environment—Our Natural Heritage" (ES&T, December 1968, page 1063).

Shortly thereafter, Sen. Henry M. Jackson (D.-Wash.) amended his bill, S. 1075. "As a nation, we have failed to design and implement a national environmental policy which would enable us to weigh alternatives, and to anticipate the undesirable side effects which often result from our ongoing policies, programs, and actions," Jackson says.

## **Sludge treatment process licensed to U.S. firm**

A process for heat-treating waste sewage sludge has been licensed to Dorr-Oliver (Stamford, Conn.) by William E. Farrer, Ltd. (Birmingham, Eng.). Like the Porteous process, introduced into the U. S. from England last year (ES&T, December, 1968, page 1068), the Farrer process relies on heat conditioning of the sludge to facilitate dewatering, without addition of chemicals; but instead of direct injection of steam, the Farrer process uses a tube-type heat exchanger and tubular reactor. Raw sludge from the thickener is ground and pumped to a preheater, where it recovers heat from previously conditioned sludge; a second heat exchanger raises the sludge temperature to 350-400° F. with a closed circuit hot water system; and a final tubular reaction chamber allows the necessary retention time to complete the conditioning. After final passage through the preheater, gravity settling can be used to produce a concentrate with 12% solids, and mechanical dewatering results in a sterile cake with 45% solids.

## **Organic solvents come under air pollution scrutiny**

A 10 member Organic Solvents Advisory Committee has been formed, according to John T. Middleton, commissioner of the National Air Pollution Control Administration (NAPCA), to advise NAPCA on the air pollution effects of organic solvents. Specifically, the committee will advise on the following items: • Techniques for assessing the contributions of organic solvents to air pollution. • Research needed to determine the relative importance of various solvents. • Methods of evaluating effects and smog-forming tendencies of solvents. • Feasibility of establishing national criteria for solvents and regulations of their use.

### **NAPCA's Organic Solvents Advisory Group**

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NAPCA

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Stanford Research Institute

Abel M. Dominguez  
Armed Forces Institute of  
Technology

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## Committee on Persistent Pesticides reports findings

“There is an immediate need for worldwide attention to the problem of buildup of persistent pesticides in the total environment,” according to the Committee on Persistent Pesticides’ report released last month. During the previous 18 months, the 15 member committee of the National Academy of Sciences-National Research Council interviewed 83 prominent experts on the subject. Under the chairmanship of James H. Jensen, president of Oregon State University (Corvallis), the committee reached 18 conclusions on pesticide uses and came up with seven recommendations. Among the recommendations are: • Steps should be taken to reduce the needless or inadvertent release of persistent pesticides into the environment. • Studies of the possible long-term effects of low levels of persistent pesticides on man and other mammals should be intensified. • Continuation of the present system of regulation, inspection, and monitoring to protect man and his food supply from pesticide contamination. Already the report, which was prepared for the U. S. Department of Agriculture, has been forwarded to the newly established Commission on Pesticides and Their Relationship to Environmental Health. Under the Department of Health, Education, and Welfare, the new commission is chaired by Emil M. Mrak, retiring chancellor of the University of California (Davis). Its mission is to evaluate all aspects of pesticide usage and make recommendations for research and policy guidelines.

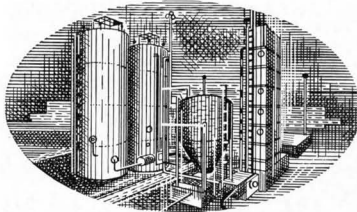
## Pesticide residues in fish are staggering . . .

Pesticides	Percentage of fish containing pesticide
DDT	essentially 100%
Dieldrin	75
Heptachlor or heptachlor oxide	32
Chlordane	22

Fish from 45 U. S. rivers and lakes contain chlorinated hydrocarbons residues, according to recent results of a two year monitoring survey, conducted by the Bureau of Sport Fisheries and Wildlife as part of the National Pesticide Monitoring Program. DDT was found in 584 of 590 samples, which included 62 species of fish. The highest DDT count, 45.27 p.p.m.—more than nine times the interim FDA tolerance level—was found in white perch taken from the Delaware River. Other rivers or lakes where the DDT levels in fish reached levels higher than 5 p.p.m. include the Apalachicola (Fla.), Arkansas (Ark.), Cooper (S. C.), Hudson (N. Y.), Rio Grande (Tex.), Sacramento (Calif.), Tombigbee (Ala.), White (Ark.), Lake Michigan, Lake Ontario, and the St. Lucie Canal (Fla.). All samples were analyzed for the presence of 11 commonly used, persistent, chlorinated hydrocarbons. The data were obtained from fish taken in the spring and fall of 1967 and 1968. Analyses were performed by five commercial laboratories, and the samples for the fall of 1967 and spring 1968 were cross-checked.

## . . . however, DDT can be removed from fish

Up to 55% of the DDT in Lake Michigan fish (ES&T, May 1969, page 419) can be removed depending on the method of preparing the food for consumption, according to biologists of Wisconsin’s Department of Natural Resources (DNR). DNR biologists compared cooked portions of fish with uncooked portions and found that deep frying reduced the DDT content by 55%, broiling reduced DDT content by 36%, pan frying-25%, and baking-11%, based on analyses at DNR fisheries laboratory (Madison). The biologists suggest discarding the cooking oil after use. The department plans additional studies on the subject.



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## **FWPCA funds operator's training programs**

Recognizing the apparent lack of qualified waste treatment plant operators, the Federal Water Pollution Control Administration (FWPCA) has awarded several contracts for training of personnel. The first grant of \$69,880 went to the State of Pennsylvania for the training of 80 operators; a second grant of \$33,048 went to Detroit Metropolitan Water Services for the training of 40 operators; and a grant of \$16,920 went to metropolitan St. Louis Sewer District for training another 20 operators. "The program is aimed at training 800 waste treatment plant operators throughout the country," says FWPCA commissioner, David D. Dominick, who noted that the majority of funds for the project is supplied by the Departments of Labor, and Health, Education, and Welfare.

## **Environmental protection department is proposed**

A new Department of Conservation and the Environment would be the federal government's single, effective instrument for the protection of the environment, according to a recent legislative proposal. Under S. 2312 the present Department of the Interior would be abolished and its primary conservation and environmental functions such as parks, recreation, and water pollution would be absorbed by the new agency. Other existing federal departments' activities such as air pollution and noise abatement also would be transferred to the new department. Introduced by Sen. Clifford P. Case (R.-N. J.), and endorsed by Sen. Frank E. Moss (D.-Utah), who introduced similar legislation in the 90th Congress (ES&T, October 1967, page 774), S. 2312 calls for a nine member Council of Environmental Advisors and an Environmental Security Council, which might, for example, be activated to deal with a major oil spill or air pollution episode.

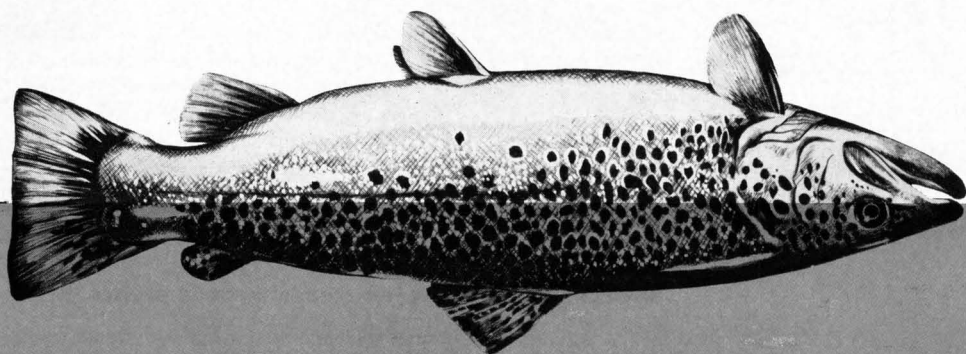
## **NAPCA offers guidelines for air quality standards**

"Guidelines for the Development and Implementation of Air Quality Standards," a recent 53-page publication of the National Air Pollution Control Administration (NAPCA), will serve to promote a broader understanding of the Air Quality Act of 1967. It will help state governments meet their responsibility under the Act. The publication is divided into several parts. Part 1 explains the provisions and the intent of the act, outlines the steps that state governments are expected to take, and identifies the factors that the Department of Health, Education, and Welfare will consider in reviewing air quality standards and implementation plans. Part 2 contains recommendations to assist state governments in developing standards and implementation plans. Part 3 describes the types of financial and technical assistance which NAPCA is authorized to provide to state, local, and regional air pollution control and air quality planning agencies.

## **U.S. and Britain to share air pollution information**

Fluid bed combustion of coal has strong potential for reducing SO<sub>2</sub> emissions. R & D information on these combustion systems will be exchanged by the U.S. and U.K. An initial three-year agreement recently was signed by NAPCA commissioner John T. Middleton, and Lord Alfred Robens, chairman of the National Coal Board of Great Britain.

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# Warm fog dispersal passes airport tests

*Seeding dispersal technique passes tests at two California airports; additional programs planned this year*

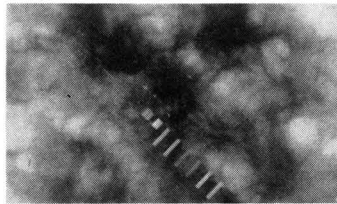
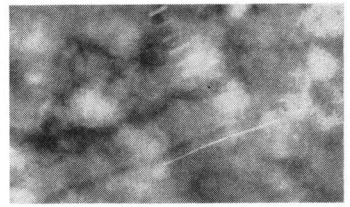


The problem of interrupted airline schedules due to low visibility ceilings—a continuing source of exasperation for air travelers and a severe drain on an airline's operating budget—appears to be yielding to modern technology. EG&G, Inc., Environmental Services Operation, a Boulder, Colo., based firm engaged in commercial-scale weather modification programs, conducted a three month warm fog dispersal program at two California airports earlier this year. The operations, conducted at Los Angeles and Sacramento airports, were aimed at seeding warm fog banks that often interrupt flight schedules in early morning hours there, in order to increase visibility to operational levels. In a recent evaluation of the program, the company concludes that the tests were "rewarding and productive, both in terms of improved seeding techniques and increased airport utilization."

Backing up the company's conviction that fog dispersal operations can result in significant economic benefit to air carriers, the company is currently expanding its fleet of fog dispersal aircraft. At the same time, EG&G is preparing proposals for conducting similar operations at eight west coast airports for this year's fog season, which usually runs from September-April.

## **Cold and warm fogs**

The California tests were directed at warm fogs, the type that are most troublesome regarding airline operations. Cold fogs—those that exist at



*Test. Photographs of NASA-CAL fog seeding experiment at Chemung County Airport, Elmira, N.Y., were taken one minute before seeding (above left), one minute after seeding began (above), and 15 minutes later (left). White line in above photo is salt plume trailed by seeding aircraft; oblong shapes are airport hangers*

subfreezing temperatures—consist of supercooled droplets that do not freeze but remain in the liquid state until they reach temperatures substantially below freezing, about  $-40^{\circ}\text{C}$ . The crystallization process can be brought about artificially, however, by introducing ice nuclei—usually pulverized dry ice—into the fog that are effective at their temperature. Cold fogs occur primarily in winter at temperatures of  $-5^{\circ}\text{C}$ . and below, and account for only 5% of all fog in the U.S. The techniques for dispersing this type of fog have been available for some time, and cold fogs have been dispersed successfully in connection with airport operations since early 1960.

Warm fogs, on the other hand, are another matter, and do not respond to

the ice nucleation seeding technique. Instead, hygroscopic materials, such as a variety of inorganic salts, are necessary. The small hygroscopic particles give up their latent heat of fusion as they take on water, and, thus, create local vertical motions in the fog cloud because the heat released warms the surrounding air. The particles also become centers for coalescence, and as the particles grow, they fall out of the fog mass.

The basic techniques applied in the California test programs, the largest warm fog dispersal experiments yet conducted, were based on basic research on warm fog seeding conducted by the Cornell Aeronautical Laboratory (CAL). These experiments showed that improvement in visibility can be

achieved under laboratory conditions by seeding with carefully controlled amounts and sizes of salt nuclei. The visibility improvement is the result of two complementary phenomenon. The initial improvement is the result of concentration of the small fog droplets into fewer drops of larger size, and a secondary improvement occurs when the drops agglomerate into a size large enough to fall out as drizzle.

The seeding material evaluated in CAL tests, and in the early phases of the EG&G California operations, was 10 micron particles of sodium chloride. The EG&G program, however, did include the evaluation of alternate seeding materials; newer information on effective particle sizes and dispersal patterns was also developed in the Los Angeles and Sacramento tests.

#### **Diversion costs**

Actually, heavy fogs occur during only about 2% of the prime air traffic hours (from 6:00 A.M. to midnight), but even so, they can be a severe financial burden for airlines. Figures from the Air Transport Association show that reduced visibility conditions at airports cost the nation's air carriers upwards of \$80 million annually. In fact, diversion of a single transcontinental jetliner from its scheduled destination can cost as much as \$20,000, mainly for accommodations and ground transportations for stranded passengers, and added aircraft service fees. These figures can be expected to rise significantly with the advent of jumbo jets of the Boeing 747 variety, scheduled to become operational in December. Aside from fog dispersal, the only other approach to reducing low-ceiling airline diversions are the so-called Category II landings, which rely heavily on radar controlled landing approaches. This technique, however, carries a high price tag—as much as \$1 million in additional electronic equipment per aircraft, plus a substantial expansion of the control tower equipment.

Faced with this situation, even a partially successful fog dispersal program could be a sound financial venture for air carriers, who eventually must foot the costs. Costs of the California test—\$80,000 for the Los Angeles operation and \$58,000 in Sacramento—were met by the respective airport authorities, but these agencies passed 90% of the cost onto the operating lines through increased landing fees.

Under terms of the contract with the two California airports, EG&G was to maintain aircraft in readiness to conduct warm fog operations when requested by the airports. Legal aspects and traffic control operations had to be coordinated with several state and federal agencies. Among the legal requirements for the program were:

- License from the state of California to conduct weather modification, after filing a description of materials to be used.

- Filing of a notice of intent to conduct weather modification with the National Science Foundation as required by P. L. 510.

- License and waiver from the Federal Aviation Administration to use nonstandard equipment in nonstandard flight patterns.

These requirements, and the development of detailed operating procedures that coordinated the activity with local traffic regulations, were completed in December of last year, and the first actual seeding operations began in January. The fog alert was maintained until Apr. 19, with seeding operations conducted as requested throughout this period.

#### **Seeding aircraft**

Five 1968 model twin engine Beech Baron aircraft were employed in the test program. They were especially equipped for the fog dispersal operation by installing stainless steel dispenser units fed from 1000 pound hoppers. Additional equipment for the missions included the necessary electronic navigational gear, including a full instrument flight regulation-equipped flight panel. A typical operational team for each airport consisted of an EG&G project manager, one pilot for each of the aircraft (two at Sacramento and three at Los Angeles), a meteorologist to supervise on-site observations and data collection, and three ground support personnel.

During the early phases of the program, the hygroscopic seeding material used was finely milled, 200-mesh sodium chloride, which had a particle size distribution of 2–60 microns with 80% in the 8–24 micron range. Seeding rate varied between 40–150 pounds per minute depending on fog characteristics. Confirming the CAL test results, this finely milled, relatively uniform size material was an efficient dispersant, but field experiences pointed to some operating problems: Because of the high ratio of small particles, it was

difficult to maintain steady seeding rates, and the uniform size resulted in a rather narrow dispersion pattern. Consequently, in the latter part of the program, material was used which has a size distribution of 2–100 microns with 65% in the 10–25 micron range. As expected, both the flow characteristics and the fallout pattern improved.

Altitude of the seeding runs depended on fog depth and wind speed. With fogs of moderate thickness—up to 500 feet—seeding runs were made at 200 feet to provide a tunnel of increased visibility, with additional runs at progressively higher altitude until the tunnel was of size to permit use of the runway for normal flight operations.

#### **Tests results**

In commenting on the specific results of the tests, EG&G spokesmen concede that the degree of success of a given operation is a subjective matter, and any improvement in landing conditions depends on such other things as landing aids available, approach obstructions, and pilot qualifications. However, evaluation of the results was based on the commonly used runway visual range (RVR) value of 2400 feet. No seeding operation was rated a success unless the initial RVR was below this value, and improvements in the RVR could be directly attributed to the seeding operations.

In all, 12 heavy fog episodes occurred at the two airports for which dispersal services were requested, in nine of which the initial RVR was below minimum requirements. In seven of the nine runs that were evaluated, takeoff or landing minimums were achieved as a result of the warm fog dispersal operations. The company further points out that 90% of the individual seeding flight requirements were usually within two hours of the fog alert call.

Larry G. Davis, manager of EG&G's Environmental Services, is also optimistic about nonairport applications of fog dispersal technology. "The same basic techniques we used in the California test can also be used to clear harbors, canals, freeways—any place where frequent incidents of warm fog disrupt the commerce of the area." A few of the possibilities are the Panama Canal, where transit through the locks is frequently interrupted for extended periods, and on major traffic arteries such as the New Jersey Turnpike, where sudden fog occurrences at times create a major traffic hazard.

# Ecological effects of pesticides assessed

*Pesticide use in Louisiana  
over the past two decades  
fortifies present need  
for concern*

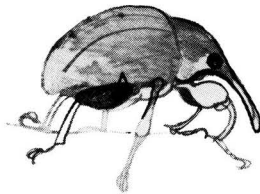
What effect 20 years of pesticide use has had on the ecology of a particular area in the U.S. has been documented by Leo D. Newsom, of Louisiana State University (Baton Rouge). His case history was presented last Dec. at a conference on Ecological Aspects of International Development, sponsored by the Conservation Foundation (Washington, D.C.) and Washington University's Center for the Biology of Natural Systems (St. Louis, Mo.).

The most enthusiastic advocates of synthetic organic pesticides agree that serious mistakes have been made in their use. Two decades of using these chemicals for control of agricultural pests in Louisiana verify that their effectiveness has been unprecedented. Louisiana's important agricultural crops—cotton, rice, sugarcane, and soybean—have all increased in size during the 20 year period.

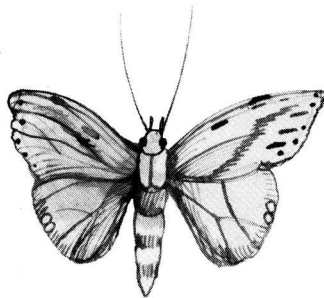
"But two decades of experience gained in the use of these controversial agricultural chemicals should allow for a reasonable assessment to be made of some of the ecological implications of their widespread use," Newsom says.

Newsom's case history does not include discussion of the impact of special pest eradication programs within the state. For example, during 1957-1962, special programs were aimed at eradication of the imported fire ant and white-fringed beetle. These programs involved one or more application per acre of dieldrin or heptachlor at a use dosage of from two to

*The complete case history will appear in "The Ecologic Boomerang," edited by John Milton and Taghi Farvar. Copyright 1969 by the Conservation Foundation and the Center for the Biology of Natural Systems. To be published by Doubleday & Co., Inc.*



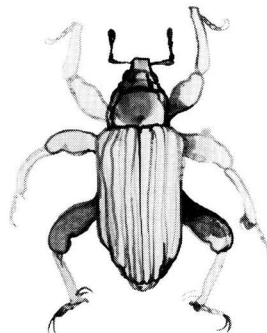
*Boll weevil*



*Corn earworm moth*



*Sugarcane borer*



*Rice water weevil*

four pounds per acre, according to Newsom's study.

More than 90% of the cropland in the state is planted for cotton, rice, sugarcane, and soybean crops. Application of pesticides in the state has resulted in the following consequences:

- Development of insect resistant populations.
- Change in status of pest species and resurgence of treated populations.
- Adverse effects on nontarget organisms.
- Pollution of the environment with persisting residues of toxic chemicals.

## **Cotton**

Perhaps, Louisiana's cotton crop illustrates best the problems associated with the use of pesticides. Large amounts of chemicals have been used to control the cotton boll weevil, a key pest of the crop. Infestations of the boll weevil in Louisiana are heavier and longer lasting than anywhere else in the U.S., so, with a possible few exceptions, more pesticides have been used in the state to control this agricultural pest than any other place in the nation. Since 1949, an estimated average of eight applications per acre per year with one or more of the chlorinated hydrocarbons and organophosphorus pesticides has been applied to all of more than 500,000 acres planted to cotton in Louisiana, the case history points out. During the period 1949-1956, calcium arsenate was used to control cotton pests, but its use was rapidly replaced by synthetic organic pesticides.

By 1955, the cotton boll weevil population had developed a resistance to chlorinated hydrocarbon pesticides. Then, the cotton and pesticide industries shifted to organophosphorus chemicals—and again succeeded in



## Estimated pesticide use in Louisiana

Pests	Pesticides <sup>a</sup>
Cotton pests, including the cotton boll weevil, bollworm, aphid, leafworm, plant bugs, and tobacco budworm	Calcium arsenate (1949-1956) Chlorinated hydrocarbons formulations <sup>b</sup> (1949-1956) Organophosphorus formulations <sup>c</sup> (1956-present)
Rice pests, including the rice water weevil and stinkbug	Chlorinated hydrocarbons formulations <sup>d</sup> (1950-1960) Organophosphorus materials <sup>e</sup> (1960-present)
Sugarcane pests, including the sugarcane borer	Chlorinated hydrocarbons materials such as endrin (1958-1967) Organophosphorus materials such as azinphosmethyl (1966-present)
Soybean pests, including the southern green stinkbug, corn earworm, and bean leaf beetle	Chlorinated hydrocarbons formulations <sup>f</sup> (1959-present) Organophosphorus materials including methyl parathion (1959-present)

<sup>a</sup> Several different formulations may have been used during any one season

<sup>b</sup> Representative formulations include the following: BHC-DDT-sulfur (0.3 lb.-0.5 lb.-4.0 lb.); dieldrin, endrin, or heptachlor-DDT (0.25 lb.-0.5 lb.); toxaphene-DDT (2.0 lbs.-1.0 lb.); endrin

<sup>c</sup> Representative formulations include the following: Methyl parathion-DDT (0.25 lb.-1.0 lb.); toxaphene-DDT-methyl parathion (2.0 lbs.-1.0 lb.-0.25 lb.)

<sup>d</sup> Representative formulations include the following: Toxaphene-dieldrin (2.0 lbs.-0.25 lb.)

<sup>e</sup> Representative materials include the following: Malathion, methyl parathion, and phosphamidon

<sup>f</sup> Representative formulations include the following: Toxaphene-DDT (2.0 lbs.-1.0 lb.)

Source: Louisiana State University, Agricultural Extension Service

controlling the pest, but not without consequences. Now, all the important pests for cotton, including the boll weevil, have populations that are resistant to one or more of the chlorinated hydrocarbon, organophosphorus, or carbamate pesticides. Cotton pests are becoming resistant faster than substitute pesticides can be found, and the situation has reached a critical stage. In one or more areas of the cotton belt, certain populations of insects can no longer be controlled satisfactorily with any currently available pesticide, according to the case history.

In Louisiana, cotton ecosystems furnish a favorable habitat for mammals, birds, reptiles, amphibians, fish, crustaceans, and insects. Some of the pesticides that have been used on cotton are incredibly toxic to some of these species. For example, several species of fish are killed by exposure to endrin at concentrations less than 1 p.p.b. Other species are relatively resistant to these materials, and some become resistant to both the chlorinated hydrocarbon and organophosphorus materials, Newsom notes.

In 1966 and 1967, soil samples collected from cotton producing areas were contaminated with substantial amounts of chlorinated hydrocarbon pesticides. The significance of these residues is not completely understood, Newsom observes.

### Rice

In Louisiana, rice is produced in an aquatic environment during much of the growing season. The rice agricultural ecosystem is extremely sensitive to the effects of pesticide application. Fortunately, rice has only two major pests, the stinkbug and the water weevil. The amounts of pesticide required to control these pests has been relatively small. The stinkbug never infests more than a small percentage of the approximately half million acres of rice planted each year. Usually, one application of an effective pesticide is all that is required for its control.

During 1950-1960, the rice stinkbug was controlled with chlorinated hydrocarbon pesticides. Usually, applications were made with toxaphene, dieldrin, DDT, or mixtures of these materi-

als. Since 1960, rice has been treated, on the average, with one application per acre per year of one or more of the chlorinated hydrocarbon and organophosphorus pesticides.

Among the more important species of wildlife which spend substantial portions of each year in rice fields are the purple gallinule, the common gallinule, the fulvous tree duck, the red crawfish, and mosquitofish. Both species of gallinule and the fulvous tree duck nest in rice fields and feed extensively on rice. At the same time, crawfish farming is an important industry of the chemically treated rice fields.

Mortality among various wildlife species was observed occasionally, but no effort was made to determine the effects of pesticide use on populations of any species in the area. Gallinules and the fulvous tree duck often were found among the dead species in the rice acreage. The chlorinated hydrocarbons, toxaphene and dieldrin, are highly toxic to many species of birds.

Substitute pesticides were sought as soon as the fish and wildlife hazards were shown. Since 1960, organophosphorus or carbamate pesticides have been used exclusively for control of the rice stinkbug. These replacement pesticides are less harmful and more economical than chlorinated hydrocarbon pesticides, according to Newsom.

But here the question of balancing various effects is noted. The extreme difficulty encountered in attempting to find pesticides that are equally safe for all species is a never ending search. Methyl parathion is the most toxic compound to crawfish of any tested.

This particular organophosphorus material is eight times more toxic to crawfish than endrin. But, at the prescribed dosage for stinkbug control, the initial concentration of the material in water would be one and one half times the maximum safe upper concentration for fish and four times the safe upper concentration for crawfish, the case history records.

The chlorinated hydrocarbon pesticide aldrin controlled the rice water weevil for the first time. Prior to 1961, control methods for this pest involved withholding water and drying the soil, a practice that is only moderately successful at best. Beginning in 1961, aldrin has been used on virtually all of the half million acres planted to rice.

Problems with the use of aldrin soon developed. Growers occasionally found dead ducks and gallinules around the field during the planting season. Now, the rice water weevil is so highly resistant to aldrin that its treatment is no longer effective. Since this resistance to aldrin was developed within five growing seasons, the recommendation for the use of aldrin on rice seed had to be withdrawn.

### Sugarcane

Until 1959, the amount of pesticide needed for control of the sugarcane borer, the only major pest of the crop, was relatively small. Since 1959, however, sugarcane has been treated, on the average, with three applications per acre per year of one or more chlorinated hydrocarbon or organophosphorus pesticides, according to the case history.

Ten years ago, endrin was hailed enthusiastically because it gave excellent control of the borer for the first time. Unfortunately, endrin is one of the most toxic materials known to many species of fish. In 1959, tremendous fish kills were observed in the streams and bayous bordering sugarcane acreage. These fish kills occurred every season thereafter, usually during July and August, until the use of endrin was drastically reduced in 1966 and virtually discontinued in 1967, the history reveals.

Other problems were also encountered with the use of the chlorinated hydrocarbon pesticides. Four years after endrin was used generally, the sugarcane borer developed a resistance to this synthetic material. In 1966, a changeover to an organophosphorus pesticide was effected. Then azinphosmethyl was used on 50% of the sugarcane acreage to control the borer; in 1967, on 90%; and in 1968, on virtually 100% of acreage planted to sugarcane.

From the standpoint of its effect on wildlife, the changeover to the organophosphorus pesticide is considerable. Azinphosmethyl is less persistent and is one fifth as toxic to bluegill as endrin, considering that the organophosphorus material is applied at 0.75 pound per acre compound to 0.33 pound per acre for endrin. At the same time, the material is 10 times more toxic than endrin to two other species in another food chain. So, the question of which species are more important in the food chain is raised. The answer simply is not available.

Another problem involves the method of pesticide application. Endrin was applied in the form of granules; azinphosmethyl is applied by emulsion concentrate spraying. As yet, no studies have been completed to evaluate the difference in potential hazard to wildlife for the two methods of application, the history notes.

### **Soybean**

From 1961-1968, the soybean, a relatively new crop, underwent a drastic intensification of production—from 197,000 acres in 1961 to 1,345,000 acres in 1968. Less than one fifth of the soybean acreage has received any pesticide application. Usually no more than two applications have been made to any of the acreage planted to this crop in one growing season.

When it became obvious that soybean production was destined to grow

into a major agricultural enterprise in Louisiana, the decision was made to develop a program of insect pest control that would not have so many of the undesirable features found in the other crop programs, the case history points out. Indeed, Louisiana's program to control soybean pests—mainly, the southern green stinkbug, corn earworm, and bean leaf beetle—is recommended to developing nations.

Soybeans that are grown on soils containing residues such as dieldrin, aldrin, heptachlor, and endrin may be expected to absorb and translocate about one tenth the present level in the soil to the plant itself. Since a zero tolerance level for chlorinated hydrocarbon residues has been set for soybeans, the presence of these residues in soil presents a potential problem.

### **Effects on fish**

No sound data is available from any source to show that there has been any permanent effect on the population of any species of fish from the use of agricultural pesticides, according to the case history. "Although it has been predicted often that one or more species would be driven to extinction by the effects of agricultural pesticides, these predictions have not come to pass," Newsom says.

"There have been no catastrophic effect on populations in Louisiana with the possible exception of catfish and frogs from the Mississippi River and its tributaries. From the same area, and during the same period of time, however, the yield of freshwater crawfish showed a tremendous increase."

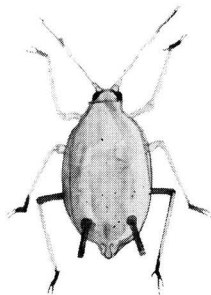
Residues of chlorinated hydrocarbons are found in a wide variety of species, often in substantially large amounts. The solubility and storage of these pesticide residues in animal fats are well known properties that make the use of these chemicals objectionable. Many believe that the concentration of these residues in food chains is the most hazardous aspect of their continued use.

The case history points out that complete information about potential hazards and storage of these materials in animal tissues simply remain unanswered. How fish that are killed by a 24 hour exposure to a pesticide like endrin at 1 p.p.b. may tolerate exposures to one fourth this amount indefinitely, and accumulate residue levels in their tissues amounting to many p.p.m., is an intriguing question that Newsom poses.

He goes on to point out that one of the most serious features about the development of pesticide resistant populations is that individuals of such populations can store much higher levels of residues than those of susceptible populations. So, resistant populations become a potential hazard to predator species. The benefits from the standpoint of survival to species having the genetic constitution which permits the development of resistant populations far outweighs the potential hazard that may be involved in the concentration of toxic residues, according to Newsom's report.

Insect residues are ubiquitous in Louisiana. The relatively large percentage of total area covered by Louisiana's agricultural ecosystems make water pollution a serious problem. During 1964, five monitoring sites were chosen for a study of pesticide residues resulting from agricultural operations, Newsom points out. Fish from all streams, with one exception, contained pesticide residues in excess of federal tolerances that have been established for meat. At the same time, water samples from the same streams from which the fish were collected failed to reveal the presence of any pesticide residues at detection levels of 0.001 p.p.m., the history reveals. But this common finding in water analysis emphasizes the rapidity and degree of adsorption of these pesticides by soil particles (ES&T, March 1969, page 207).

During 1961-1964, one team of investigators made a deliberate attempt to measure endrin concentration in surface waters which drain 3300 acres of sugarcane. Endrin could not be found at levels higher than parts per trillion in water samples but at concentration level of parts per billion in bottom sediments.



*Cotton aphid*



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# Odors from industries need controls

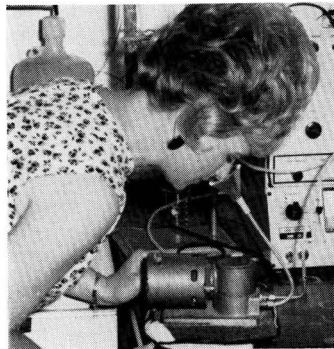
*Several companies tell of their experiences in abating malodors, while other projects seek the chemical constituency of diesel engine fumes*

Odors from buses, aircraft, rendering plants, sewage plants, and industrial operations in general are obvious nuisances. Most people complain about these emissions, and rightly so. But studies conducted by one company and several research groups hold promise for some relief from odor burdens.

Rhodia, Inc. (New York City), is in the business of correcting malodors. Rhodia offers a system (Chemscreen) which can be used for in-plant and out-plant odor problems. Specifically, Rhodia makes available nine counteractants which can be used to neutralize malodors from specific industrial and municipal operations. Rhodia, an important chemical company, is a major producer of aromatic chemicals. The company's expertise in counteracting malodors is backed by 10,000 formulations for odor correction. A number of industries have availed themselves of Rhodia's services, using Chemscreen agents to solve their industrial odor problems.

The Long Island Lighting Co. (LILCO) (Mineola, N.Y.) put Rhodia know-how to work to solve an oil odor problem associated with the transfer of oil from tankers to the utility's storage tanks. At its Northport Power Station, LILCO has three large oil storage tanks, each with a capacity of 12 million gallons. At its Port Jefferson Power Station, the utility has a single oil storage receiving tank with a 6 million gallon capacity. In the pumping of large volumes of oil from tankers to these tanks, the air from the tanks is replaced. This replaced air contained the oil odors which prompted the complaints.

Rhodia equipment and Chemscreen agent were positioned atop each storage tank. "The first equipment was



**Sniffing.** In a mobile lab, subjective odor reactions are noted

placed on top of a tank at the Northport Station before the summer of 1968," says Michael C. Ascher, an engineer in the utility's mechanical and civil engineering department. "Since that time, the same type of equipment and agent have been placed on top of all storage tanks. Actually, installation for the last tank will be completed this month," Ascher elaborates. "Since the first unit was installed, complaints from the local citizenry have been significantly reduced," he concludes.

Frequently, odor complaints are made against a sewage treatment plant by area residents. Located in an industrial area, the Metropolitan Denver Sewage Treatment and Disposal Plant (Colo.) received such complaints during this past spring, apparently originating from 16 acres of lagoons constructed on the plant site.

"The lagoons were constructed as a temporary measure and will be phased out by midsummer 1969," says Jerold D. Wingart, Metropolitan's plant manager. "To effectuate odor control, the plant mixed one chemical with all

materials pumped to the lagoons and employed the Rhodia system around the periphery of the lagoons." But Wingart stressed that complete odor control will be accomplished by the impending elimination of all lagoons.

All ingredients of the Rhodia formulations are on the generally recognized as safe (GRAS) list of the Flavoring Extract Manufacturers' Association of the U.S. (Washington, D.C.). Rhodia's equipment (Rho-D-Air) features a vaporizer which converts the specific liquid counteractant into a gas at a continuous flow rate. The gas then is induced into air ducts, released through properly designed orifices, and forms an air screen. By placing the duct system for release of the gas at strategic industrial sites, the malodor would have to pass through the barrier of counteractant. In so doing, the malodor is neutralized, resulting in elimination of both the odor and the public complaint.

## Odor programs

A number of projects in odor identification are in progress at Arthur D. Little, Inc. (A. D. Little), Illinois Institute of Technology Research Institute (IIT), and Southwest Research Institute (SWRI). In general, the projects run for three years, and first year results are becoming available. "All aim to correlate odors with specific organic compounds, but positive correlations have not been possible to date," says George D. Kittredge, spokesman for the National Air Pollution Control Administration (NAPCA). "Each project operates at a funding level of approximately \$100,000 per year," Kittredge says. He indicates that, while NAPCA initially did not participate in the funding of the IIT program, the agency



**Touring.** Southwest Research Institute's mobile lab will be used to measure 2500 subjective reactions to odors in five major U. S. cities

soon will be contributing to the support of all three projects.

The A. D. Little (Cambridge, Mass.) project is attempting to find the specific constituents of diesel odors which are responsible for human odor responses at the p.p.b. or lower concentration levels. "In this project, the diesel odor was described by the odor profile method," says John T. Funkhouser, program director. "This method permits the odor to be characterized by odor notes—kerosene, burnt, and oily. Then, as the odor sample is further purified, panel members can determine whether the odor has remained unchanged. Results of the first year of this project indicate that odor components can be identified by this approach. Hopefully, by the end of the program, the major components of these diesel odor notes will be identified as individual chemicals," Funkhouser concludes.

Initiated in Feb. 1968, the A. D. Little study was funded by American Petroleum Institute (API), NAPCA, and the automobile industry, through the Coordinating Research Council (ES&T, February 1968, page 87; November 1968, page 993), Kittredge notes.

The project at IIT Research Institute (Chicago, Ill.) is similar to the A. D. Little program in that it, too, involves a technical panel of odor specialists. However, the IIT plan differs both in sampling technique and general approach. "This study involves the actual collection of diesel odor field samples, which are collected on an adsorbent at ambient temperatures," says Andrew Dravnieks, director of the project. "Then, samples are regenerated, and the odor components separated by analysis in a specially designed two column gas chromatographic apparatus. Members of the odor panel can sniff individual odor components as the components are eluted from the column. In this way, subjective reactions can be recorded for each component."

"To date, the estimated number of components ranges from 1000-2000," Dravnieks says. "Only a fraction of these are really strongly odor relevant. Of the large number of components, approximately 10 elicit a very strong response from members of the panel. Most of these components appear to be aldehydes. Some other components must be present in certain combinations in order to elicit a response from panel members. Next year's program will attempt to further identify and characterize these components that elicit a strong response," IIT Research Institute's project director elaborates.

In its first year (May 1968-May 1969), the IIT project was funded by API and the automobile industry. Now, NAPCA has joined in financial support of the \$100,000 program.

Southwest Research Institute (San Antonio, Tex.) has two odor programs underway, according to NAPCA's Kittredge, with each program wholly funded by NAPCA. The first, an 18 month program, commencing June 1968, is funded for a total of \$118,000. "The aim of this program is to design and construct a mobile trailer laboratory which would be used to find the man-in-the-street's reaction to typical odors representative of many urban environments," says Karl J. Springer, SWRI program director. "The trailer would be moved from location to location so that different nontechnical groups of subjects could shed some light on odor nuisances. Initially, the trailer will be moved to five sites in the San Antonio area, then to Chicago at another five sites, then to Los Angeles, and eventually to two other cities," Springer explains. "Approximately 100 persons will be tested at each site for a total of 2500 participants for the project. National Opinion Research Center (Chicago, Ill.), a consultant to this study, prepared the questionnaire and will evaluate the public opinion data," Springer adds.

SWRI's second project, entitled, "Investigation of Diesel Powered Vehicle Odor and Smoke," is entering its fourth year of operation," says NAPCA's Ralph C. Stahman. "This project operates at a funding level of \$80,000 per year."

"We are using the Public Health Service's methods for measuring smoke and odor," says SWRI's Springer. "Techniques for odor and smoke reduction include engine modifications, catalytic mufflers, fuel additives, and the like. At this point, we haven't hit on anything that will significantly reduce odor emissions. Recently, a six month test was completed, but no promising lead has appeared. In the upcoming year, engine modifications and catalytic mufflers will be emphasized for significant odor control reductions," Springer concludes.

#### Legislative proposals

Odor control and abatement requirements now are being included in state legislative proposals and rules. These proposals and rules do not name specific objectionable odors, and generally are phrased in nontechnical terms. "West Virginia's Regulation 4, one of the first odor regulations in the U.S., became effective Oct. 1, 1967," says Carl G. Beard II, director of the West Virginia Air Pollution Control Commission. According to Regulation 4, "No person shall cause, suffer, allow, or permit the discharge of air pollutants which cause or contribute to an objectional odor at any location occupied by the public."

Another legislative proposal to cope with odor nuisances is before the Illinois state legislature. On Apr. 28, House Bill No. 2770 was introduced by state representative J. Theodore Meyer and cosponsored by Ralph T. Smith, speaker of the Illinois House of Representatives. Section 8 of this bill reads, "The control division shall enforce any laws enacted by political subdivisions pertaining to the emission of objectionable odors within its jurisdiction. An objectional odor is any odor which is objectional to at least 15% of the registered voters in the political subdivision."

After passage by the executive committee of the Illinois legislature, (15 yeas to six nays), the bill was passed by the House in a 124 to 12 vote, according to Charles J. Ryant, Jr., technical consultant to the legislative study committee. Now the bill has been sent to the Senate.

# NAPCA checks emissions of new autos

*Before new cars are sold in the U.S., manufacturers must assure the federal government's certification facility of compliance with emissions standards*

Some 10 million 1970 model automobiles will be sold in the U.S. Nationwide; automotive vehicle emissions account for 60% of the air pollution burden. But in certain cities the percentages are much higher. On the east coast, for example, in Washington, D. C.—an area practically devoid of industrial operations—approximately 80% of the air pollution is due to the automobile. On the west coast, Los Angeles has controlled industrial emissions from stationary sources but still is faced with an air pollution problem. Here again, approximately 80% of Los Angeles' air pollution burden is due to the automobile.

Historically, Title II of the 1965 amendment to the Clean Air Act of 1963 gave to the Secretary of Health, Education, and Welfare (HEW) the authority and responsibility to develop standards for the control of motor vehicle emissions. Present federal law requires domestic and foreign automobile manufacturers, who plan to sell their products in the U.S., to test their vehicles in accordance with the regulations promulgated by the Secretary of HEW. By meeting these control requirements, domestic and foreign automobile manufacturers make sure that their products measure up to applicable federal regulations, thereby reducing pollutant emissions from motor vehicles.

HEW operates a certification facility to verify that the degree of control specified for automobile emissions is achieved. The federal government's certification facility (Ypsilanti, Mich.) is under the direction of Kenneth D. Mills, acting director of the National Air Pollution Control Administration's (NAPCA) Division of Motor Vehicle Pollution Control (DMVPC). Within



**High emissions.** NAPCA facility tests vehicles with high performance engines, manual transmissions, and multiple carburetors, which have significantly higher emissions than conventional automatic transmission vehicles

NAPCA's Bureau of Abatement and Control, DMVPC is responsible for the following functions:

- Certification of present and future model year vehicles.
- Development of test procedures.
- Evaluation of advanced emission control technology, including alternate power sources.
- Development of surveillance procedures.
- Collection of surveillance data.

## Controls

Two generations of federal standards for motor vehicle emissions controls have been promulgated—one for 1968 model vehicles and a second for

1970 model vehicles (1969 models are covered by the '68 regulation). For 1968 model vehicles, NAPCA issued 886 certificates of conformity for light duty vehicles, mainly automobiles. Actually, the facility performed 730 tests for certification purposes. At a private independent laboratory, these tests cost approximately \$200-\$300 each. For 1969 model vehicles, NAPCA conducted 1083 tests at its Ypsilanti facility and issued 956 certificates of conformity. "For 1970 model vehicles, more than 1000 tests will have to be performed for some 850 conformity certificates," Mills projects.

"The '68 standard was a concentration type standard with adjustments

for reduced exhaust volumes from vehicles equipped with small engines," Mills says. This standard is based on three engine sizes—from 50-100, from 100-140, and greater than 140 cubic inches displacement (CID) engines.

The 1970 federal standard changed from a concentration standard to a grams per vehicle mile standard. While this standard—written in terms of mass emissions—is a much closer approximation to equitable emissions from all vehicles, still there is room for improvement. It won't be until the third generation of regulations comes along in 1972 that a true mass emissions standard is possible.

#### Procedure

Manufacturers' vehicles are grouped according to engine classes—each class consists of all engines of the same displacement. Each manufacturer—with DMVPC approval—selects four representative vehicles from his product line for each engine class and collects emissions data on this fleet of automobiles.

Starting as a general rule with the 1968 model certification procedure, two criteria were used in the selection of these test vehicles: the likelihood of high emissions and representativeness of sales.

Test vehicles are driven 4000 miles and then tested at the manufacturer's facility. For example, the 225 CID engine, which is used in Chrysler Corporation's Valiant, Barracuda, Belvedere, Fury, Dart, Coronet, and light duty truck product lines, would be tested as one engine class. Chrysler's emissions data fleet for the 225 CID engine class might consist of one Valiant, one Fury, one Coronet, and one light duty truck. The remainder of the fleet would be made up of similarly selected vehicles for each class of engines produced by Chrysler Corp.

Although the manufacturer only tests four vehicles in each engine class, NAPCA may certify as many as 20 different product models based on data from these tests. If the average emissions of the four test vehicles multiplied by a deterioration factor meet the federal standards, then NAPCA certifies all of the manufacturer's product line with that size engine.

Domestic manufacturers maintain two separate fleets of cars, according to Louis V. Lombardo, technical assistant to NAPCA's assistant commissioner for standards and compliance, William H. Megonnell. The cars in the dura-



**Evaporative losses.** Required tests for evaporative emissions control on 1970 and 1971 model vehicles takes 13 hours at Michigan facility

bility fleet are not the same as those in the emissions fleet.

The durability fleet, a second fleet of between four and ten test vehicles, also is selected by the manufacturer based on NAPCA criteria. In the durability data fleet, the manufacturer drives the vehicles, testing them at 4000 mile increments until 50,000 miles are accumulated on each vehicle. Emissions are measured for each 4000 mile increment up to 50,000 miles. From these data, a deterioration factor is calculated. A factor of unity indicates that the emissions from the vehicle did not change over 50,000 miles and should not change appreciably during the lifetime of the car—assumed to be 100,000 miles—except in the event of a major failure.

Frequently, however, the deterioration factor is larger than unity. A deterioration factor of 1.20, for example, indicates that the emissions are 20% higher at the end of 50,000 miles than at 4000 miles. But, the emissions still must be within the 1968 standards or NAPCA's certification of conformity would not be granted.

Each manufacturer submits his data and test vehicles to the certification facility where NAPCA conducts confirmation tests before issuing the certificate of conformity. Only this confirmatory testing is performed at the

Ypsilanti facility for each fleet of test vehicles.

#### Heavy duty vehicles

For the first time, with the 1970 standard, emission controls are required on heavy duty engines used in buses, trucks, and the like. In addition, new diesel engines must meet an exhaust smoke opacity standard equivalent to a light haze. The 1970 standard also imposes restrictions on the concentration of hydrocarbons and carbon monoxide in the exhaust of gasoline-fueled heavy duty engines.

At present, NAPCA does not have the facilities for testing heavy duty engines at its Ypsilanti facility, Mills notes. To issue compliance certificates, NAPCA personnel visit the manufacturer's facility, scrutinize and review his data and test facilities, observe smoke tests, and pass on them.

Automobile manufacturers routinely announce their new vehicles in September. So, a lead time of 12 months is involved in the actual testing and collecting of data for certification. For example, from Sept.-Dec. 1968, the testing of the manufacturers' emissions fleets for 1970 vehicles and the generation of data were conducted by the manufacturer. Concurrently and extending on to Mar. 1969, the manufacturers collect data on their dura-

### Cumulative reductions in motor vehicle emissions released to the atmosphere

	(millions of tons)					
	1966	1967	1968	1969	1970	1971
Hydrocarbons	1.3	1.8	2.8	3.9	5.2*	6.9*
Carbon monoxide	0.4	0.9	5.8	11.2	18.1	25.0

\* Effect of California's 1970 evaporative control standard is not included

Source: NAPCA

ability fleet of vehicles. By Apr.-July 1969, all data obtained by the manufacturers and NAPCA on both fleets will be reviewed.

Then—as early as possible, but before the manufacturers actually begin to sell the 1970 model vehicles—NAPCA issues the certificates of conformity, the majority of them during the months of June and July, according to Lombardo.

### Revised test procedure

NAPCA has drafted a new test procedure for 1972 model light duty vehicles. The procedure has not been published in the *Federal Register*, but a draft has been circulated to automobile manufacturers for their comments. "For the first time, the 1972 standard will be a true mass emissions standard," says Thomas A. Huls, acting chief of the procedures branch.

The 1968 standard for exhaust emissions are expressed in concentration units. In the 1968 procedure, exhaust gases were sampled continuously, and the concentration of pollutants measured in parts per million, but the exhaust volume was not measured. Not only is the concentration of pollutants important, but total volume of exhaust gases is needed to arrive at a true mass emissions. And concentration times volume is the mass, Huls notes.

The 1970 emissions standards are expressed in mass emissions terms of grams per vehicle mile and are calculated from two factors:

- Concentration of emissions.
- Exhaust volume (calculated from an empirical relationship based on vehicle weight).

By use of these factors, the 1970 standard achieves a closer approximation to a true emissions standard than the 1968 standard.

### DMVPC's Mills



The proposed 1972 procedure measures the actual mass of exhaust emissions that leave the tail pipe. The mass of emissions will be measured by allowing exhaust gases coming from the tailpipe of the vehicle to flow through a constant volume sampler. "When one measures the concentration that goes through the constant volume sampler and multiplies it by total flow (a fixed value) the mass of emissions is obtained," Huls explains.

The 1970 test procedure underestimates the actual exhaust emission. "We are finding that emissions actually are 60% or more higher than those calculated by the 1970 procedure," Huls says. One reason for the discrepancy is that the empirical exhaust volume calculation was based on hot operation of the engine. During cold operation and warm-up of the engine, the exhaust volume rate is higher than during hot operation, Huls notes. So, the emissions data during warm-up of the vehicle are higher in the 1972 emissions procedure than in the 1970 procedure, even though the vehicle emission characteristics are unchanged. Also, the 1972 procedure includes additional operating modes and start-up.

### Promising control techniques

A number of promising control techniques are being evaluated by automobile manufacturers, according to Ralph C. Stahman, acting chief of DMVPC's emission control engineering branch. These include:

- **Exhaust gas recirculation.** This technique is being evaluated in a long-term feasibility program. In addition to maintaining reduced hydrocarbons and carbon monoxide emissions, control of NO<sub>x</sub> emissions appears feasible. "The cost for this type of control would be approximately \$10-15 per vehicle," Stahman says.

- **Air injection.** This technique is expensive but promises up to 90% control of hydrocarbons and carbon monoxide emissions. In this technique, air is mixed with the exhaust gases in the exhaust manifold where combustion of exhaust components occurs. Air injection systems are primarily used on high performance vehicles, usually equipped with manual transmissions. Ford's air injection system (Thermactor) is used on several models, such as the Mustang and the Cougar.

- **Exhaust manifold reactors.** "These devices are still several years away," Stahman says. "The reactors now used have a materials problems and do not

withstand the high temperatures involved."

- **Stratified charge engine.** A new form of internal combustion is being investigated under a NAPCA contract with the U.S. Army Tank Command and Ford Motor Co. In the Ford combustion process engine, the fuel charge is injected into the cylinders and directed specifically at the spark gap. In addition to low hydrocarbons and carbon monoxide emissions, this technique may provide a reasonable basis for NO<sub>x</sub> control. "Six or seven years of engineering work by Ford have already gone into this alternate power system," says Stahman. "Unexpectedly, we are finding that particulate emissions may be a problem."

- **At present, DMVPC has a staff of 50 people and operates at a funding level (fiscal year 1969) of \$2.3 million,"** says Mills. Two thirds of the money goes for support of the present facility and one third goes for contracts. Sixty percent of the people are professionals, the remainder are technicians and other support personnel. "We look forward to expansion in fiscal year 1970. Assuming that the budget request of \$2.7 million is approved, DMVPC plans to increase to a total of 75-80 personnel," Mills says hopefully. "In fiscal year 1970, \$1 million is needed for equipment, and another \$1 million will be needed for equipment in fiscal year 1971. In five years, the division may need from 235-240 persons and require an annual budget of \$6.3 million."

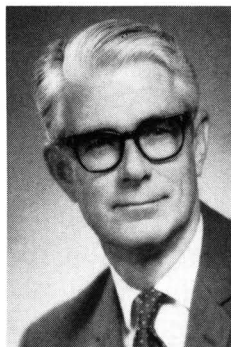
### Future effects

What effect these controls and test facilities will have on the future U.S. air pollution burden still is uncertain. Although standards became effective for the first time with 1968 model vehicles, the public will not be able to notice any effect until 1970, nor any downturn in emissions until 1971. Current standards will only improve the situation in the short run. Even with a projected slight downturn in emissions after 1971, the relief will be short lived, according to NAPCA estimates. An increase in vehicle population and vehicle usage will again begin to increase pollution levels by late 1970. The downward trend only holds true for hydrocarbons and carbon monoxide. Neither lead compounds nor oxides of nitrogen are included. These pollutants will continue to increase the air pollution burden until standards are set for them.



# A Symposium—The Technical Significance of Air

## Ambient CO levels may be no immediate health threat — but what about aesthetics?



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The practical control of urban carbon monoxide concentrations is generally recognized as being analogous to its control within repair garages, and must be achieved by diminishing the gas emitted to the air by automobiles and other vehicles. Unlike the cars in a garage, however, emission of exhaust gases to the atmosphere cannot be controlled by ventilation, so more difficult expedients must be attempted. Such efforts have increased greatly in recent years and now, of course, maximum concentrations have been established by law, and the prospect is that these levels will be steadily lowered.

Unlike the case of most other air contaminants, this imposition of emission standards for carbon monoxide has preceded the issuance of air quality criteria or standards, even though such ambient air levels are assumed when setting emission standards. The federal government will be issuing such criteria soon, however, and a number of states have already set maximum permissible levels of carbon monoxide, presumably to protect public health. California has been most thorough in its effort to establish a sound basis for carbon monoxide standards, as well as other standards, and has published extensive documentation of supporting information. In other instances, however, the basis has been less thorough.

### Exposure to carbon monoxide

In spite of the very extensive literature on the subject, it is nevertheless true that many questions can be asked

concerning the effects of breathing air containing carbon monoxide at relatively low concentrations (less than 50 p.p.m.)—questions which are not readily answerable. Recently, Bartlett has reviewed low level exposures, and has done an excellent job of defining areas for further investigation. Dinman covered somewhat the same area, but concerned himself more specifically with probable effects of continued exposure on populations at special risk—for example, those afflicted with coronary artery disease, congestive heart failure, pulmonary disease, and so on. A bibliography through 1965 of publications dealing with carbon monoxide was issued by the U.S. Public Health Service; it contains nearly 1000 entries, with abstracts, more than half of which are related to biological effects. It is obviously impossible to summarize all of this information, but several observations are pertinent.

In normal, healthy, individuals the rate at which carboxyhemoglobin forms in the blood and the rate at which it dissociates are well established. Saturation levels are a function of concentration, and decrease markedly as concentrations are lowered to ambient urban levels. Several years ago, we performed a simple study which confirmed the substantial time for equilibrium to be reached when nonsmoking volunteer subjects were kept in a 30 p.p.m. carbon monoxide environment. The subjects, healthy males, engaged in light activity or rested for a 24 hour period in which time carbon monoxide levels averaged 30.2 p.p.m., and never

varied by more than 3 p.p.m. Carboxyhemoglobin levels in the blood rose to an anticipated high of 5% saturation in about 12 hours; a relatively rapid increase was followed by a long period of gradual increase to the saturation level. Thereafter, no further uptake of carbon monoxide occurred. Although not determined in this study, release of carbon monoxide proceeds in similar fashion.

The rate of uptake and release of carbon monoxide by the blood has a direct bearing on the selection of air standards. It is apparent that short exposures to high levels may not result in significant blood level alterations, in contrast to the relatively rapid response to an irritant gas such as ozone. The uptake and release rates themselves do not define the effects of the blood-carbon monoxide combination, and it is obvious, on the basis of Dinman's and Bartlett's reviews, that the effects of chronic exposure need clarification.

It is particularly important that the effects on specialized nervous system functions at carboxyhemoglobin levels below 5% be studied much more intensively. Several investigators have observed effects on the perception of time by animals, and on the performance of psychomotor tasks by humans. On the basis of the known effects of carbon monoxide, it is difficult to select a level which may be tolerated for extended periods of time by the entire urban population of a city. There does not appear to be adequate justification purely on the

*(Continued on page 634)*

## Reactivities of smog components are central issue in setting control standards

**T**he two principal types of urban air pollution currently recognized are:

- **The chemically reducing type**, derived largely from the combustion of coal and oil, in which sulfur dioxide is an important constituent, and which is mixed with soot, fly ash, smoke, and partially oxidized organic compounds.

- **The chemically oxidizing type**, called photochemical smog, in the formation of which sunlight plays an important role. This smog is practically free of sulfur dioxide but contains substantial amounts of nitrogen oxides, ozone, ozonated olefins, and organic peroxide compounds, together with hydrocarbons of varying complexity.

While both types are widely distributed (but are not always clearly defined), the first type has been closely associated with London; the second—with which this paper is concerned—with Los Angeles.

### Oxides of nitrogen

Nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) are the major oxides of nitrogen (NO<sub>x</sub>) produced during combustion. The other nitrogen oxides are relatively minor in amounts and effects.

Nitric oxide is formed by direct combination of oxygen and nitrogen in air at high temperatures. In ambient air at ordinary temperatures, NO is slowly oxidized to NO<sub>2</sub>, using light energy absorbed by the brown nitrogen dioxide gas which is thereby dissociated to nitric oxide and monatomic oxygen. The latter also produces ozone by combining with O<sub>2</sub>.

Nitrogen oxides react in the atmosphere with organic compounds, particularly hydrocarbons, to produce formaldehyde, acrolein, ketones, aldehydes, acids, and also ozonides, ozonated olefins and peroxyacetyl nitrate and its analogs—peroxy-propionyl nitrate, peroxy-butyryl nitrate, peroxy-isobutyryl nitrate, and peroxy-benzoyl nitrate. The latter are exceptionally active air pollutants which injure vegetation and are strong eye irritants.

The oxides of nitrogen have been monitored in California and elsewhere; the atmospheric concentrations of nitrogen dioxide and nitric oxide in large American cities range from 0.04-0.66 p.p.m. The highest concentrations—about 0.5-0.6 p.p.m. nitric oxide and 0.2-0.4 p.p.m. nitrogen dioxide—are found in Los Angeles. The nitric oxide maximum occurs between 7-9 A.M. and from 4-6 P.M., and is apparently associated with peak traffic. The concentrations fall off during the day due to oxidation to nitrogen dioxide, but remain fairly high in the evening until midnight when a second minimum occurs and persists until morning. The nitrogen dioxide concentrations also respond to the traffic peaks and are high and variable during the day and lowest at night at about one third the nitric oxide level. The morning nitrogen dioxide peak occurs at about 10 A.M., one to two hours after the nitric oxide peak.

The phytotoxicity of nitrogen dioxide has recently been found to be much greater than earlier experiments indicated. Previous data showed that

exposure to 10-20 p.p.m. nitrogen dioxide for several hours was required to injure alfalfa, grains, and sensitive weeds; newer data show injury at lower levels for other plants:

- **Tomato seedlings**—2.5 p.p.m. in four hours.

- **Pinto bean seedling**—10 p.p.m. for four hours.

- **Tobacco**—acute injury in 8.7 hours at 2.3 p.p.m., but not by 2.4 p.p.m. in five hours.

- **Tomato and bean seedlings**—inhibited in growth by 0.3-0.5 p.p.m. applied continuously for about 10-20 days.

### Ozone

Ozone is another powerful oxidizing compound characteristic of photochemical urban pollution. Ozone can be formed by photochemical reaction between nitric oxide, nitrogen dioxide, and oxygen in the atmosphere, and by reactions of these oxides with hydrocarbons to form organic smog compounds. Ozone causes the cracking of rubber under stress; in fact, an analytical method for ozone is based on the extent of this cracking under controlled conditions. Four automatic analyzers are available for determining ozone in the atmosphere:

- **The Littman-Beniolli recorder**, which uses potassium iodide solution.

- **The Kruger ozone photometer**, in which the gas absorbs ultraviolet light at 2537 Å.

- **The galvanic cell ozone-bromine recorder.**

- **The Mast recorder.**



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### Discussion by:

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## Ozone

Ozone is phytotoxic, causing upper-surface necrotic flecking, stippling, and mottling on plant leaves at concentrations as low as 0.1-1.0 p.p.m. for one to several hours. Pinto beans, for example, show moderate leaf damage at 0.2 p.p.m. in two hours, and duckweed (*Lemna minor*) shows a reduction to 40% in chlorophyll content and photosynthesis rate after fumigation with 0.2 p.p.m. ozone for 24 hours. Tobacco is particularly susceptible to ozone injury, which has been observed in the area from North Carolina, Maryland, and Connecticut to Canada. Flecking, which renders cigar wrapping leaves worthless, usually develops following exposure to 0.05 p.p.m. (by Mast), but 0.02 p.p.m. can also cause fleck. In an experiment in Beltsville, Md., tobacco plants of an ozone-susceptible variety (Bel W<sub>4</sub>) grew 94% larger in 34 days in carbon filtered air than in ambient air.

Animal ozone toxicity data indicates that 0.1-3.0 p.p.m. can cause bronchitic pneumonia, edema, and mortality in a few hours in mice, rats, and guinea pigs. Humans are adversely affected by 0.3-0.5 p.p.m.

Recently, D. Reiss, at the Medical Center of the University of Colorado at Denver, and others, studied animal lung tissue which was treated directly with ozone and nitrogen dioxide. Ozone had a much greater effect on the tissue than nitrogen dioxide. The gases reacted with the surface layers of the lung and penetrated to the cell interior, stimulating cell division and causing an increased production of carbonyls. The gases also increased the capacity of bacteria to cause pneumonia in the lungs.

## Peroxy-acyl compounds (PAN)

In reactions between nitrogen oxides and such olefins as pentene-1 and butadiene, irradiation by ultraviolet light promotes splitting of the olefin at the double bond. One end of the bond forms a carbonyl compound; the other end reacts with the nitrogen dioxide to form a very reactive peroxy-acyl compound that is eye irritating and plant damaging. Five analogs have been prepared, in which the acyl radical is either acetyl, propional, butyryl, isobutyryl or benzoyl. Up to 210 p.p.b. of the acetyl compound, PAN, is present in Los Angeles smog, and as much as 50-60 p.p.b. in other California cities. The other analogs are present

in lower concentrations but they are 4-100 times more reactive. The benzoyl compound has only recently been prepared and has not yet been studied extensively, but it appears to be the most reactive. It is said to be 200 times more eye-irritating than formaldehyde.

PAN causes glazing and bronzing of the lower surface of sensitive plant leaves, and also causes tissue collapse, chlorosis, and leaf drop. It attacks the sulfhydryl group in leaf enzymes and has produced visible symptoms with 14 p.p.b. in about four hours. Leaf injury is confined to areas of a specific physiological stage of development on rapidly expanding portions of the leaf. Minimum light and dark periods are required before, during, and after fumigation treatment to cause injury.

Another group of powerfully oxidizing organic compounds in the Los Angeles atmosphere are the ozonated olefins. They are somewhat less phytotoxic than ozone itself or the PAN analogs. The initial work on the production of phytotoxic organic compounds in the Los Angeles atmosphere was carried out by Haagen-Smit.

## Organic pollutants in the atmosphere

Both gaseous and particulate organic compounds are present in the atmosphere. Nonvolatile organic solids or compounds strongly adsorbed on the surfaces of solid particles account for a great many organic pollutants of diverse properties and effects. Some of the polynuclear hydrocarbons, such as benzo-a-pyrene, have carcinogenic properties. These materials have been studied extensively by Sawicki and his group in Cincinnati and by Dubois, Monkman, and their coworkers in Ottawa. Their methods have been particularly useful in determining the concentrations of the carcinogenic compounds in the atmosphere as well as many other nonvolatile organic compounds.

These compounds can be collected on 20 by 25 cm. glass fiber filters at an air sampling rate of about 80 m.<sup>3</sup>/hr. to yield a sample weight of about 250-350 mg. The sample is extracted with benzene or cyclohexane, filtered, and evaporated to dryness in the dark at 70° C. The 50-150 mg. residue is dissolved in chloroform, dispersed in alumina and the chloroform evaporated. The dry powder is transferred to the top of a chromatographic column, and the column is eluted with a pentane-diethyl ether mixture. Each

successive 100 ml. of solvent has an increased percentage of diethyl ether, and about 40-50 fractions, each 15-20 ml., are collected in test tubes on a fraction collector. The fractions are evaporated to dryness in the dark in a vacuum oven. The solid in each tube is dissolved in pentane and transferred quantitatively to a 3-ml. spectral cell having a 1-cm. light path.

The ultraviolet-visible absorption spectrum from 2200 Å-4500 Å is determined for the samples, and results are compared with spectra from known concentrations of each pure compound. Some of the polynuclear hydrocarbons fluoresce strongly and can be measured by fluorescence also.

Organic compounds in auto exhaust and coal and oil combustion products can be determined by any of several detector systems. The hydrogen-flame analyzer is particularly effective because it measures ionization of the carbon atoms in aldehydes, ketones, alcohols, amines, and hydrocarbons, without interference by carbon dioxide, carbon monoxide, oxygen, nitrogen, or moisture. The response of the detector is converted to millivolts by an electrometer and recorded in the range of 0.1 mv. with a one-second response time.

In a typical flame ionization detector about 75 ml./min. of a mixture of

## Urban air may contain wide range of hydrocarbons

Hydrocarbon	Expected concentration range (p.p.m.)
Methane	1.6-10.0
Ethane	0.05-0.50
Propane	0.05-0.40
Isobutane	0.05-0.30
n-Butane	0.05-0.45
Isopentane	0.05-0.35
n-Pentane	0.05-0.35
Ethylene	0.012-0.25
Propene	0.001-0.10
Butene-1	0.001-0.02
Isobutylene	0.001-0.01
trans-2-Butene	0.0005-0.01
cis-2-Butene	0.0005-0.01
1,3-Butadiene	0.0005-0.01
Acetylene	0.015-0.25
Propylene	0.005-0.05
Benzene	0.01-0.05
Toluene	0.01-0.05
Ethyl benzene	0.002-0.02
Xylenes	0.01-0.1
C <sub>9</sub> + aromatics	0.01-0.2

Source: Altshuler, A. P., "Atmosphere Analysis by Gas Chromatography," U.S. Department of Health, Education, and Welfare, Public Health Service, Division of Air Pollution, 1969; California Department of Public Health, SDPH1-SPDH 1-50 (Aug. 1966)

## Ozone's toxicity to animals<sup>a</sup>

Ozone concentration (p.p.m.)	Exposure Conditions	Results
<b>Mice</b>		
1.0	30 hrs. per wk. for 62 weeks	Chronic lung injury
1.34	Short exposure	Disturbance of conditioned reflexes
2.7-4.5	2 hours	Bronchitis and pneumonia
<b>Rats</b>		
2.4	Repeated exposure	Hemorrhage and edema
1.0	6 hr. with exercise	6 out of 10 dead
1.0	19 hours	Reduced weight gain of young rats
<b>Guinea pigs</b>		
1.0	30 hr. per week for 62 weeks	Chronic lung injury; increased mortality
0.25-0.50	30 hr. per wk. for 17 weeks	30% increase in mortality
0.10-0.20	30 hr. per wk. for 24-35 weeks	20% increase in mortality
<b>Humans</b>		
0.3-0.5	Long periods	Respiratory irritation and headache
0.40	30 minutes	Discomfort and irritation

<sup>a</sup> Freebairn, H. T., *J. Applied Nutrition*, 12 (1959)

nitrogen (60%) and hydrogen (40%) is burned in about 350 ml./min. of hydrocarbon-free air plus 0.5-10 ml./min. of the sample containing the hydrocarbon. The detector is extremely sensitive. Concentrations less than 1 p.p.b. can be determined if a freeze out trap is used to concentrate the hydrocarbon.

Considerable study has been devoted to remedial measures to be taken in Los Angeles to alleviate smog effects, particularly eye irritation. Korth, Rose, and Stahman have studied the effects of various concentrations of hydrocarbons and oxides of nitrogen such as may be found in auto exhausts. Hydrocarbons ranged from 3-12 p.p.m. carbon and the NO<sub>x</sub> from 0.25-2.0 p.p.m. Irradiation time was 120 minutes. Their results show that:

- A decrease in the HC/NO<sub>x</sub> ratio reduced reaction rates and produced less complete reaction.

- Increase in initial hydrocarbon concentration increased the NO<sub>x</sub> formation rate to a maximum at 1 p.p.m. NO<sub>x</sub>.

- Oxidant formation increased with hydrocarbon concentration and decreased with NO<sub>x</sub>. Below a 3:1 HC/NO<sub>x</sub> ratio there was no free oxidant in the system at equilibrium.

- The percentage of NO<sub>x</sub> reaction increased with increasing initial hydrocarbon concentration above the 3:1 HC/NO<sub>x</sub> ratio.

- Average NO<sub>2</sub> concentration increased through a maximum as the hydrocarbons fell from 12 to 3 p.p.m. With further decrease in hydrocarbon concentration, NO<sub>2</sub> decreased also.

- Increased hydrocarbons increased eye irritation. An increase in NO<sub>x</sub> above 0.5 p.p.m. increased eye irritation to a maximum at 1 p.p.m. NO<sub>x</sub>, then decreased it to 2 p.p.m.

- Plant damage required a minimum concentration of 30 p.p.h.m. oxidant.

- NO<sub>2</sub> formation rate is limited at 120 minutes.

Evidently, the foregoing reactions are complex but first require a reduction in the HC concentration to about 3 p.p.m., then a simultaneous reduction of both HC and NO<sub>x</sub> below 3 p.p.m. and 1 p.p.m., respectively, to avoid eye irritation and plant damage.

### Discussion

**Winner:** Dr. Thomas has presented a bird's-eye view of the complex phenomenon known as photochemical smog. In any such condensation, different points of emphasis will attract different people. Two areas from Dr. Thomas' paper appear to be especially important at the present time.

As Dr. Thomas has noted, nitric oxide is discharged into the atmosphere by combustion processes as a result of the high temperatures involved. This touches a point often neglected in discussing nitric oxide as a contaminant. Unlike air pollutants which originate from imperfections in the combustion process, nitric oxide is a basic and necessary product of efficient power production in internal combustion engines. This element of necessity is sometimes disputed on the basis that parameters can be found where nitric oxide formation is minimal; however, fundamental studies clearly indicate that such conditions

do not produce efficient conversion of chemical energy to mechanical work. Hence, any control on the production of nitric oxide effectively places a lid on engine efficiency and the hidden cost inherent in this situation could be quite high. Before controls in this area are actually implemented, they deserve careful consideration.

The fact that nitric oxide control is likely to be expensive is, in itself, no reason to refrain from such controls if they produce sufficient benefits. In considering the benefits, it is important to recognize that the role of nitric oxide in smog is a dual one—it is both a primary reactant in and an inhibitor of atmospheric reactions. At low concentrations, an increase in nitric oxide increases reaction rates and product yields; however, above a certain concentration, further increases reduce reaction rates and yields, and the dominant role changes to that of an inhibitor. The concentration where this changeover occurs depends on the concentration and kind of hydrocarbon present. Such complex behavior makes it extremely difficult to assess benefits attributable to any given reduction in atmospheric nitric oxide. Nevertheless, at least four literature references conclude that nitric oxide reductions would be relatively ineffective in reducing photochemical smog symptoms. There are, of course, contrary viewpoints.

The direct effects of nitric oxide must also be considered in assessing the benefits that would accrue to its reduction. Although most authorities agree that direct effects of atmospheric nitric oxide are unimportant, its oxida-

## Nitrogen oxide concentrations in urban air

Year	1964-65 averages in p.p.m.				
	Month	Day	Hour	5 min.	
<b>Nitrogen dioxide</b>					
Max. in 6 Cities	0.050	0.063	0.14	0.37	0.66
Avg. for 6 Cities	0.038	—	0.065	0.14	0.18
Avg. for 31 Cities	0.050				
Avg. for 37 Cities	0.044				
<b>Nitric oxide</b>					
Max. in 6 Cities	0.098	0.144	0.33	1.02	1.19
Avg. for 6 Cities	0.051	—	0.12	0.36	0.43

Source: U.S. Department of Health, Education, and Welfare, Public Health Service, Division of Air Pollution, Cincinnati, Ohio (1966)

tion product, nitrogen dioxide, is toxic to both humans and plants. Dr. Thomas reports that 0.3 p.p.m. induces detectable growth retardation in certain plants; 2 p.p.m. will produce acute injury in a few hours. In man, nitrogen dioxide produces a threshold odor response between 1-5 p.p.m., and acute effects appear at about 13 p.p.m., with longer-term effects from intermittent exposures to 3-10 p.p.m. By way of comparison, Dr. Thomas reports that in six cities studied, the maximum five minute average concentration of nitrogen dioxide was 0.66 p.p.m. with a maximum daily average of 0.14 p.p.m. Hence, ambient levels of nitrogen dioxide appear to be several fold too low to do direct harm to man or plants.

This suggests that the benefits from nitric oxide controls on internal combustion engines are rather nebulous; on the other hand, the cost to the public is likely to be very concrete.

### Hydrocarbons

Dr. Thomas did not examine the fact that different hydrocarbons participate to markedly different degrees in atmospheric photochemical reactions. At one extreme is methane, which is generally regarded as non-reactive, while olefins with internal double bonds react vigorously. As shown by Dr. Thomas, both are present in the atmosphere, as well as many compounds with intermediate reactivities. Thus, the hydrocarbon component of photochemical smog is a complex mixture of individual compounds, each possessing different chemical properties with respect to the reaction system involved. A reduction in the quantity of hydrocarbons emitted will not necessarily insure a proportionate reduction in photochemical smog. Although this situation has long been recognized by the technical community, disagreements on classifying hydrocarbon reactivity have

prevented its recognition in emission control regulations.

These disagreements arise from the diversity of reaction parameters and biological effects which can be used to classify the reactivities of hydrocarbons. Reactant conversion rates, product formation rates, product yields, eye irritation, plant damage, and materials damage can all be used. Many workers have concluded that the relative reactivities depend markedly on the parameters; others, using essentially the same evidence, have concluded that most parameters yield similar rankings of hydrocarbon reactivities. Our own studies suggest that substantial agreement exists among reactivity parameters as long as hydrocarbons with unrealistically high reaction rates are excluded. Hydrocarbons having more than twice the reaction rate of exhaust hydrocarbons, taken as an aggregate, were considered as outside the range of realism in these studies. More recent work by Heuss and Glasson has indicated a significant degree of association among most chemical parameters; eye irritation, however, did not correlate with any of the chemical parameters. These latter data suggest to us that the lack of correlation between eye irritation and the chemical parameters may well have resulted from the nature of these specific eye irritation measurements and the particular chemical parameters chosen for comparison. If so, other chemical parameters and other methods of measuring eye irritation may show association. The question would then reduce to whether eye irritation methods that are realistic with respect to the atmosphere show association with chemical parameters. Some time will pass before this question can be answered. Nevertheless, even the crudest accounting of reactivity differences would represent a significant step forward from regulations based

only on the quantity of hydrocarbons emitted.

**Altshuller:** One statement in Thomas' discussion of NO<sub>x</sub> emissions is subject to misinterpretation. Analyses of automobile and diesel exhaust as well as of effluents from stationary sources clearly show that almost all of the nitrogen oxides present exist as nitric oxide, not nitrogen dioxide. This is important, because it means that nitrogen dioxide is present as a result of atmospheric, not combustion reactions.

I am unaware of any atmospheric analyses proving that ozonides or ozonated olefins are present as air pollutants. Such products may be formed under certain laboratory conditions in studies of olefin-ozone reactions. However, in our laboratory we have not been able to show that such substances exist as stable gas-phase products in the low range of concentrations.

My coworkers and I have reported that, in laboratory photooxidations, hydrogen peroxide and alkyl hydroperoxides are significant products of aldehyde photooxidations using solar radiation conditions.

Dr. Thomas includes peroxybenzoyl nitrate in his list of plant damaging agents. While it may appear reasonable, on a structural basis, to postulate that peroxybenzoyl nitrate is a phytotoxicant, I am unaware of any experimental results that support this possibility. I would be interested in learning of any such results.

With specific reference to nitrogen dioxide dosages and the adverse effects of nitrogen dioxide, several aspects need additional discussion:

- \* The toxicity of ozone appears to be about 10 times that of nitrogen dioxide, according to Coffin.

- \* The plant damage results summarized by Dr. Thomas indicate that 10-100 times more nitrogen dioxide than ozone is needed to cause injury to various plant species.

- \* In the cities in which continuous air monitoring is conducted under National Air Pollution Control Administration (NAPCA) auspices, concentrations obtained are much less than those found to cause biological effects. In fact, the concentrations reported for nitrogen dioxide, except at some of the monitoring locations in the Los Angeles basin, rarely ever reach the levels accepted in California as causing coloration effects. There also is no experimental evidence in

## Most photochemical smog constituents are phytotoxic

	Plant	Conc. (p.p.m.)	Exposure time	Effect
<b>Nitrogen dioxide<sup>a</sup></b>	Bel B-W3 tobacco	2.4	4 days	No injury
	Tobacco	2.3	8.7 hours	Acute injury
		2.4	5.0 hours	No effect
	Tomato Seedlings	2.5	4 hours	Acute injury
		0.5	10 days	Growth inhibition
	Sensitive weeds	20.0	1 hour	Acute injury
	Pinto bean seedlings	10.0	4 hours continuous	Acute injury
		0.3-0.4		Growth inhibition, but no necrosis
<b>Ozone</b>	Bean	0.4	20 min.	Acute injury
	Duckweed	1.0	4 hours	5% reduction in photosynthesis
		1.0	24 hours	38% reduction in photosynthesis
		0.2	24 hours	40% reduction in photosynthesis
	Pinto bean	0.2	2 hours	Moderate to acute injury
	Valentine bean	0.12-1.0	½ hr.-3 wks.	Necrotic leaf spots
	Bel B tobacco	0.8	1 hour	27% acute injury
	Bel W3 tobacco	0.8	1 hour	72% acute injury
	Lemon seedling	0.25	40 hr. per wk. for 9 wks.	Increased sugar, decreased starch, no acute injury
<b>Ozonated olefins<sup>c</sup></b>	Bean	0.4	4 hours	Acute injury
	Duckweed	0.2	1 hour	Acute injury, reduced photosynthesis
<b>Peroxyacetyl nitrate<sup>d</sup></b>	Bean	1.0	15 min. (dark)	No injury
		1.0	15 min. (light and dark)	Acute injury
		1.0	3 hr. after fumigation	Acute injury

<sup>a</sup> Benedict, H. M., and Breen, W. H., 3rd National Air Pollution Symposium, Pasadena, Calif. (1955); Taylor, O. C., and Eaton, F. M., *Plant Physiol.*, **41**, 132-135 (1966)

<sup>b</sup> Heck, W. W., and Dunning, J. A., *J. Air Poll. Control Assn.*, **17**, 112-114 (1967); Heggstad, H. E., *J. Air Poll. Control Assn.*, **16**, 691-694 (1966)

<sup>c</sup> Jaffe, L. S., *J. Air Poll. Control Assn.*, **17**, 38-42 (1967)

<sup>d</sup> Dugger, W. M., et al., *J. Air Poll. Control Assn.*, **13**, 423-428 (1963)

these cities of the presence of nitrogen dioxide at any time at both the concentrations and pathlengths computed to cause coloration effects. Nor am I aware at present of direct experimental evidence for the p.p.m.-mile levels of nitrogen dioxide computed to cause coloration effects. We now are supporting work on open-path optical techniques which will include measurements of nitrogen dioxide concentrations over long atmospheric pathlengths.

I must disagree with the statement in Dr. Thomas' background document that "more recent studies have shown that reduction of organic substances is *futile* in reducing eye irritation without a corresponding reduction of nitrogen oxides." Nicksic and his co-workers, in their statistical treatment of a variety of irradiation chamber results reported in 1964, do not conclude that the results support the need for nitrogen oxide control. Instead, these authors say, "There is very little support, if any, in the data for action that would interfere with implementation of hydrocarbon controls, as is now proceeding. . . ." The experimental results obtained in NAPCA laboratory studies up to the present support this conclusion by Nicksic, Harkins, and Painter. In addition, the eye irritation

measurements we have made lead to the following conclusions:

- Little, if any, eye irritation has been obtained with varying amounts of NO<sub>x</sub> up to above 1 p.p.m. in the absence of added organic substances.

- Little eye irritation is measured when paraffinic hydrocarbons are irradiated with NO<sub>x</sub>. Thus, selective removal of olefins and alkylbenzenes by emission control systems or by fuel modification for evaporation loss control should be effective in reducing eye irritation.

- Concurrent reduction of reactive hydrocarbons and NO<sub>x</sub> at constant ratio conditions does not appear any more effective than hydrocarbon control alone.

Reduction of hydrocarbons to low levels without reduction of nitrogen oxides also reduces oxidants, peroxyacyl nitrates, and aldehydes. Thus, the bulk of experimental work indicates that all adverse manifestations of photochemical air pollution except nitrogen dioxide dosage are much reduced by hydrocarbon control. Our experimental results also indicate that nitrogen dioxide dosages, on the average, will either not be changed significantly or will be somewhat decreased by a high level of hydrocarbon control.

I have been concerned for several years about the lack of effort to apply techniques used successfully in irradiation chamber studies to investigations of photochemical reactions in urban atmospheres. Efforts are in motion to remedy this deficiency; one can hope that these studies will be useful in making the critical and costly decisions involved in pollution control.

NAPCA is vitally concerned with promulgation of control measures which technical results show to be most effective in reducing adverse effects of air pollution. What now is essential is quantitation of the relationships between varying degrees of reduction of emissions to reduction of adverse effects on receptors under atmospheric conditions. One way of expressing such considerations is to emphasize cost to benefit comparisons for varying levels of control of reactive hydrocarbons or nitrogen oxides or both in relation to adverse effects. We all wish to obtain the maximum benefits to the public for the minimum cost to the nation. Such conclusions cannot be achieved on the basis of good intentions alone. We need the best possible experimental results handled by the finest statistical techniques and introduced into realistic systems analysis procedures.

(Continued from page 628)

basis of health effects to support a standard more stringent than the serious level of 30 p.p.m., over an eight-hour period, adopted by the State of California.

Although safeguarding human health should be the principal purpose of a standard for carbon monoxide, I should like to offer the opinion that other considerations suggest that 30 p.p.m. for eight hours is excessive, and that some lower concentration should be considered a more desirable measure of true air quality for most communities. Carbon monoxide in community air is, for all practical purposes, a diluted vehicular exhaust product, and it is impossible to elevate carbon monoxide levels without at the same time elevating levels of most other exhaust components, or the products into which they are converted in the atmosphere. I believe that this single consideration is most important, for studies of toxicity and other effects normally use pure carbon monoxide, and although the conclusions are sound, they may not represent the effects of an air-carbon monoxide mixture breathed by the inhabitants of a city.

#### Monitoring data

An air pollution study sponsored by the U.S. Public Health Service at our laboratory near the center of downtown Detroit illustrates this point. For more than four years, several gases were continuously sampled and analyzed by automatic recording instruments at our laboratory. The data show that the air at this location is comparable to urban air elsewhere, containing varying amounts of several gases as well as particulate matter. Because the laboratory is near two streets carrying substantial traffic loads, vehicular exhaust is a significant component of the pollutant burden, but I expect the data would be similar in most other central city locations. The close relationship between traffic flow and carbon monoxide concentrations is clearly shown in two peaks, at 8:00 a.m. and 4:00 p.m., which reflect diurnal traffic variations.

Increases in the concentrations of  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{NO}$ , and  $\text{CO}_2$  as carbon monoxide levels increase are clearly observed. In the case of  $\text{NO}$ , probably most closely related to carbon monoxide as an exhaust gas, the increases are quite dramatic. Carbon monoxide and  $\text{NO}$  concentrations vary linearly,

clearly indicative of simple dilution as the controlling factor.

No simple relationship exists for the other gases, but all increase as carbon monoxide levels increase—even  $\text{SO}_2$ , not a significant constituent of exhaust gases, tends to be higher. So, to some extent, carbon monoxide behaves as an index of air quality, or, assuming a constant rate of emission, as an index of urban ventilation, or lack of it. As I recall, the highest carbon monoxide concentrations which persisted for one or more hours were the result of stable atmospheric conditions, rather than unusual traffic densities. Visibility reduction was such that most would agree that the air was dirty or hazy.

I have not analyzed other data to corroborate our findings, but I suspect that such an analysis would support the belief that the physiological effect of pure carbon monoxide is not the controlling factor in establishing criteria or standards. On the basis of present evidence, the selection of a single limiting concentration of carbon monoxide for extended time periods is difficult. But whereas 30 p.p.m. appears adequate from health considerations, carbon monoxide is inevitably a component of air which is more pollutant-laden than should be accepted. I am aware of no evidence that the levels of  $\text{NO}$ ,  $\text{NO}_2$ , or other gases which accompany elevated carbon monoxide levels are in themselves harmful, or whether the entire mixture is harmful at such levels, for that matter. Neither is there much evidence that it is not harmful, particularly if sustained for several days. On aesthetic grounds, however—the obvious desire of everyone for clean air—air containing 30 p.p.m. carbon monoxide is dirty, and a lower concentration, perhaps 15 p.p.m., is preferable as a standard.

#### Important variables

Certain qualifications, common to all air contaminants, bear examination to clarify what is actually meant by a 30 p.p.m., 15 p.p.m., or any other standard. Important variables must be specified before any number has meaning: the more obvious are sampling location, duration of sampling, and the accuracy of the methods.

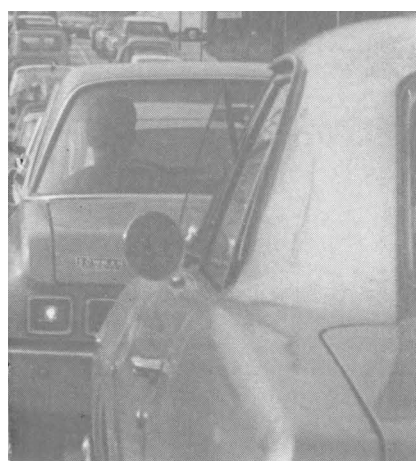
In the case of carbon monoxide, proximity of the sampling point to traffic, and traffic density are obviously important and controlling factors. Without defining all possible time and concentration conditions, it seems clear that one standard must be concerned



with the general level of carbon monoxide, a standard not directly influenced by adjacent traffic, being essentially that level which any city dweller in a certain area must breathe if outdoors. It is this kind of a standard that I suggest ought to be consistent with the desire of the community for clean air. I suspect that 15 p.p.m. is such a realistic standard.

Many people who drive, walk, work, or even live close to heavy traffic would experience exposure to substantially higher than normal levels of carbon monoxide, and several factors must be considered in regard to such persons. The exposure of cab drivers, truck drivers, traffic policemen, and so forth, is occupational and, hence, subject to control by measures applicable to all industrial workers. For example, the threshold limit value concept can be applied to the exposure of such individuals, and a daily time-weighted average exposure of 50 p.p.m. would be permissible. Industrial hygienists should evaluate such exposures and recommend adequate control measures.

Pleasure drivers normally do not spend many hours exposed to the higher CO levels frequently recorded on our streets and freeways, and any standard designed to protect such drivers would logically be appreciably higher than the community air standard, in recognition of the importance of exposure time. The same is true of pedestrians and others casually exposed to street levels of carbon monoxide, but those who live immediately adjacent to busy streets must be afforded the same guarantee of air quality as other residents. Carbon monoxide levels measured in a moving car, or at curbside, will not prevail within a dwelling, however. Exhaust concentrations diminish rapidly with



distance, and, in addition, most residences are not in equilibrium with outside air. I believe that residences usually contain less of the common pollutants than the air around them, with obvious variations related to the degree of ventilation which the householder may elect.

#### Analytical methods

One final area of concern is the sampling and analytical method or apparatus used to establish the actual carbon monoxide levels. A great many chemical and physical methods are theoretically capable of quantitatively determining carbon monoxide in air—the U.S. Public Health Service bibliography contains more than 150 entries on this subject—but not many methods are suited to measuring low ambient levels continuously. This situation is not unique to carbon monoxide, of course, and in recognition of this problem, the Inter-Society Committee on Manual of Methods for Ambient Air Sampling and Analysis was formed several years ago, in which seven professional societies concerned with air pollution are seeking to select, standardize, and test the most suitable methods.

No standard methods have yet been released, but in the opinion of the subcommittee on carbon monoxide, the most useful method for carbon monoxide analysis is by means of commercially available, nondispersive infrared instruments sensitized for carbon monoxide. They offer the advantages of continuous recorded data, adequate sensitivity and specificity, and relatively trouble-free operation. Their only shortcoming is high cost, which tends to limit the number of potential users and the locations which may be sampled at one time.

There are no other commercially

available recording instruments which the subcommittee considers suitable for ambient air analysis, and, hence, several manual methods are of interest as standard methods. The first, also an instrumental infrared method, uses a conventional laboratory infrared spectrophotometer rather than a nondispersive instrument. In addition, a 10 meter gas cell is required so that concentrations as low as 10 p.p.m. may be measured. Because of the relative insensitivity of this method of analysis, it is not useful in monitoring carbon monoxide concentrations at many locations, and in addition, it is difficult to analyze large numbers of samples.

Another carbon monoxide method under consideration is a colorimetric procedure requiring only an ordinary spectrophotometer and common laboratory glassware. It is a manual method, based on the reaction of carbon monoxide with an alkaline solution of the silver salt of *p*-sulfaminobenzoic acid to form a colloidal suspension of silver. According to Levaggi and Feldstein, the minimum detectable concentration is 5 p.p.m.

There are many other means of measuring carbon monoxide, but some are insensitive, are inaccurate at low levels, or have not been developed commercially. Perhaps the most widely used method of carbon monoxide determination is the indicating tube through which a small volume of air is drawn by means of a squeeze bulb pump. The most popular of these devices uses an impregnated gel—developed by the National Bureau of Standards—which changes color from yellow to shades of green and blue. As normally used, reading errors may be substantial, and low concentrations are estimated with some uncertainty.

#### Discussion

**Weinstock:** Dr. Smith's argument that the air quality standard for carbon monoxide be lowered from 30 p.p.m. for eight hours to 15 p.p.m. for eight hours implies that the 30-p.p.m. standard is not conservative enough. However, the 30-p.p.m. California standard was intended to be very conservative, established to protect the most sensitive population group—people with emphysema, anemia, or severe heart disease. This standard was based on aviation medicine studies where altitude hypoxia is the analogous problem. A reduction in atmospheric pressure reduces oxygen in the hemo-

globin and this condition, although more severe biologically, was equated to low blood hemoglobin resulting from reaction with carbon monoxide to form carboxyhemoglobin. Exposure to 30 p.p.m. CO results in 5% carboxyhemoglobin in the blood, which corresponds to an altitude of 6000 ft. This 30-p.p.m. standard was also set below the equivalent aviation standard as a safety factor; if it is to be lowered further, a new medical basis will have to be found.

#### Criteria for control

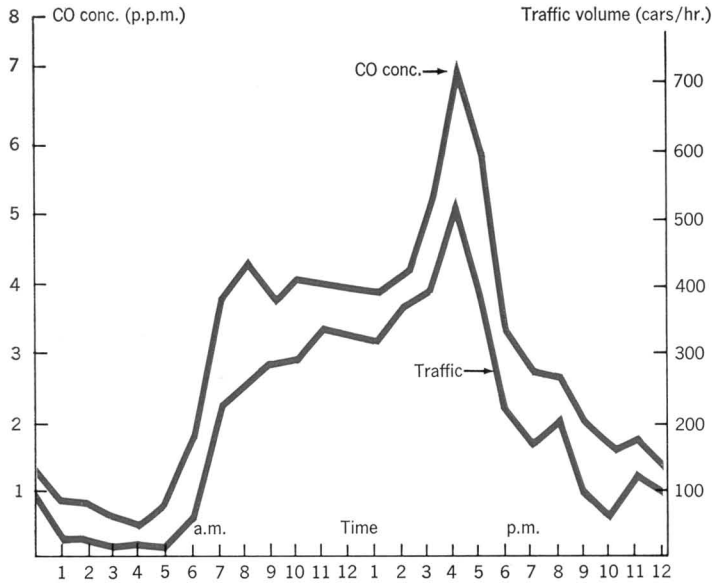
The purpose of air quality standards is to provide criteria for air pollution control. For carbon monoxide, the problem is simple because motor vehicles are the source of 85% of carbon monoxide emissions. Accordingly, California in 1966 restricted cars sold there to an average emission of 1.5%. (Emissions from cars at this time ranged from 3.2–3.5%.) This requirement was effected nationwide for 1968 vehicles; this criterion will probably be reduced to 1% for 1970 models, and Jean Schueneman, [then] Chief of the Criteria and Standards Development Program for NAPCA has stated that this must be reduced to 0.5% by 1975.

These measures suggest that air quality with respect to carbon monoxide is very poor. However, a frustrating aspect of this attitude is the difficulty in finding data that show that this 30 p.p.m.-eight hour standard is often exceeded. For example, in Dr. Smith's 1962–65 study, the highest average concentration for one hour was only 33 p.p.m., and the average concentration exceeded 30 p.p.m. only 0.05% of the time, 4.4 hours in a year. The 15-p.p.m. level was exceeded only 0.66% of the time, or 59 hours in the year. If these periods persisted for eight hours, this would still only give concern for seven days in the year.

It can be argued that Detroit is not a severe enough test. However, additional data were taken in 1967 in midtown Manhattan by the New York City Department of Air Pollution Control. Instruments were housed in a trailer on 45th St. one half block west of Lexington Ave. The sampling probe was 15 feet above the pavement and 5 feet from the curb. (A number of other sites were measured but values from this site were the highest.) Here, on the average, carbon monoxide concentration persisted at 17



## CO levels mirror diurnal traffic peaks



Source: 1962-65 monitoring survey in Detroit, Mich.

p.p.m. for eight hours—well below the 30 p.p.m. standard, but above 15 p.p.m. However, I think the introduction of the 1968 model cars with 1.5% carbon monoxide control will decrease these values, ultimately by a factor of 2. The reason is that it is impossible to imagine that car densities in midtown Manhattan could be increased. Air quality there should be nearly proportional to the emissions per vehicle and not to the total car population. In any case, it follows that for New York City to argue for carbon monoxide control, it would be necessary to lower the standard well below 30 p.p.m. New York State has under consideration a standard of 15 p.p.m. for eight hours for 15% of the time.

### Carbon monoxide vs. air quality

This brings us to Dr. Smith's major point. Some downtown city streets can be unpleasant places, and odor and dirt and motor vehicles contribute to these conditions. But these unpleasant aspects can not be attributed to carbon monoxide, which is odorless, tasteless, and colorless. And carbon monoxide evinces no biological symptoms until rather high levels of carboxyhemoglobin are reached. To argue that carbon monoxide control will improve air quality in these respects is unjustified, but this is an attitude generally accepted in this country.

Dr. Smith is correct in observing

that carbon monoxide and the nitrogen oxide levels are related, but incorrect when he states that improving air quality for CO may improve it for other pollutants. For the nitrogen oxides the opposite could occur. Studies on the relationship between nitrogen oxide and CO emissions show clearly that a reduction in CO emissions achieved by running the engine lean (higher air/fuel ratio) will result in higher nitrogen oxide emissions. Without elaborating on these complex problems, I can assure you that extensive engineering and research programs are being devoted to them.

### Long-term effects

Another concern about carbon monoxide is the long term ecological problem. Since CO is relatively unreactive, there is the worry that it will accumulate in our atmosphere and that its growing concentration may adversely affect the balance of nature. This is a most serious question to answer, and could provide a sounder reason for CO emission levels than the medical basis.

Data for downtown Los Angeles, where air pollution is the most severe in the country, relate to this question. I have analyzed such data—reported in the *Clean Air Quarterly* published by the California Department of Public Health—to compare carbon monoxide levels with total gasoline consumption. The 12 month average

trend of the peak and maximum hourly average CO concentration (for each month) for downtown Los Angeles was plotted for the period 1958–68, as well as the gasoline consumption in Los Angeles County. In view of the saturation effect, I expected the maximum hourly levels to remain relatively constant over the years rather than increase and then to decrease in late 1965 with the introduction of 1.5% CO emission controls on the 1966 cars. I was more than surprised at what I found—no correlation with gasoline consumption. A rather steady drop during 1961–62 is not readily explainable, and I do not want to speculate on possible explanations. But the expected break with the 1966 model cars appears quite clearly, being particularly sharp for the yearly average momentary peak values observed each month—even these have dipped below 30 p.p.m.

### Global concentration

The extensive air quality data taken in California relate mainly to the rate of emission of CO into the atmosphere and do not answer the question of whether the global concentration of carbon monoxide is increasing with time. What we would like to know is the chemical half-life of CO in the atmosphere. This can be estimated from the average global concentration and the rate at which it is being introduced into the atmosphere. The first estimate of this type was made by Bates and Witherspoon in 1952 in a paper that appeared in the *Monthly Notices of the Royal Astronomical Society*, "The Photochemistry of Some Minor Constituents in the Earth's Atmosphere." They took the average global concentration of CO to be 0.1 p.p.m. from astronomical observations, and, from their estimated rate of CO production, decided that this level would be reached in about 2.5 years. A 1967 evaluation by Robinson and Robbins of the Stanford Research Institute reached essentially the same conclusion, although they made extensive use of low level atmospheric CO measurements in remote areas. These estimates support the view that CO has a short half-life in the atmosphere, although an important question remains: What is the actual mechanism of CO removal?

CO half-life in the atmosphere can also be derived from radiocarbon dating. Wolfgang and his coworkers showed that, when radiocarbon is

formed, the hot carbon atom is fixed chemically as carbon monoxide rather than as carbon dioxide. Thus, conversion of  $^{14}\text{CO}$  to  $^{14}\text{CO}_2$  is another measure of the half-life of carbon monoxide in the atmosphere, and Wolfgang and his coworkers have done such an experiment. With the assistance of the Linde Air Products Co., they measured the specific activity of CO samples separated from liquified air as well as the concentration of the CO in the air samples. The characteristic conversion time of CO to  $\text{CO}_2$  was 0.1 year. One can take some assurance that the global concentration of CO will not increase disastrously.

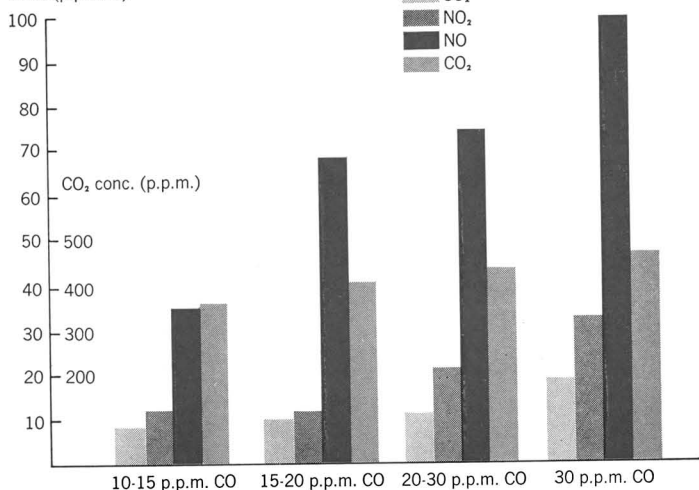
### CO in the biosphere

The final question is whether CO is really foreign to the biosphere. G. V. Pickwell of the Naval Undersea Warfare Center has studied a class of jellyfish known as siphonophores, of which the Portuguese Man-of-War is a familiar member. Some of these marine creatures abound in thick layers at 50–100 meter depths. Their presence, and the constant stream of bubbles they produce, interfere with naval sonar gear. These bubbles come from the pneumatophores, or swimming members of the organisms—part of their method of locomotion is for the siphonophore to inflate the pneumatophores' sacs with a gas that Pickwell has shown to be pure carbon monoxide. J. W. Swinnerton and his group at the Naval Research Laboratory have confirmed this phenomenon by measuring the CO concentration of the ocean as a function of depth. Their findings include remarkable maxima, rising to two orders of magnitude above the saturation concentration, that show the ocean to be a source of CO in these areas. While a quantitative estimate of the emission rate has not been made, it is reassuring to see that carbon monoxide has had an extensive role in the biosphere long before the industrial revolution.

This may be a good time to re-evaluate our attitudes about carbon monoxide. The 1.5% control on automotive exhausts should provide an improvement; if a further reduction to 1% is imposed, it should dispel any real environmental concern about CO for the foreseeable future. Whether to lower the air quality standard of 30 p.p.m. for CO to 15 p.p.m. is really not the crucial question. Instead, we must ask ourselves whether all reduction of air pollutants is desirable and

### Levels of all major pollutants rise with CO increases

$\text{SO}_2$ ,  $\text{NO}_2$ , and NO  
conc. (p.p.h.m.)



**Index.** The above data are based on mean hourly concentrations obtained during a 1962-65 monitoring survey in downtown Detroit, Mich. The increase in levels of all major pollutants leads Smith to believe that, in one sense, CO behaves as an index of air quality

can certainly do no harm. For carbon monoxide, this attitude is probably unjustified and greatly complicates the problem of dealing with the other undesirable motor vehicle emissions, and could result in our paying an excessive economic penalty for the benefit achieved. I do not mean to imply that our government officials are unaware of, or unconcerned with, the economic and engineering balance that should be achieved—from personal experience, I know that they are not. However, I do believe that a public attitude of excessive concern about carbon monoxide has developed which would support any measure of carbon monoxide control.

**Wilkening:** The establishment of criteria for carbon monoxide is an unexpectedly complex matter in light of the recently rediscovered fact that the physiologic effects of carbon monoxide, at low levels, need further elucidation. Dr. Smith points out the infinite number of factors to be considered before reasonably valid quantitative criteria are possible. Anyone who has made continuous quantitative measurements of urban carbon monoxide concentrations can vouch for the wide variation in peak concentrations and the profound effect of traffic density, sampling location, and micrometeorology on the recorded levels. We also agree that the nondispersive infrared

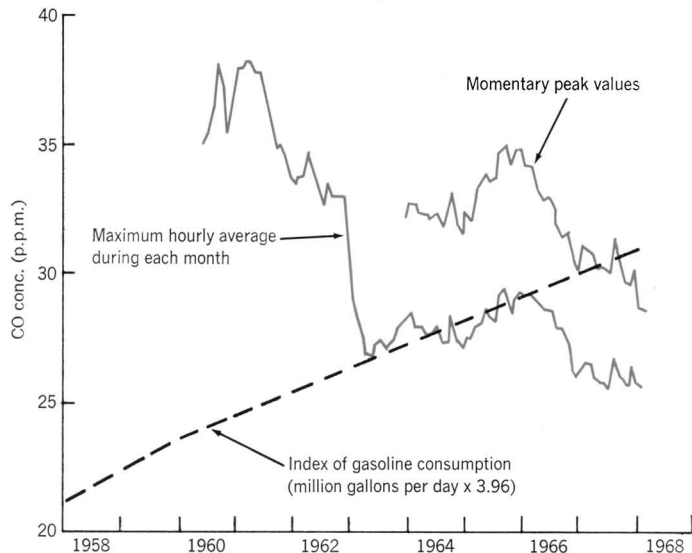
instruments are currently best suited for continuous measurement.

The correlation of carbon monoxide concentrations with physiologic effects observed in man has offered support for the contention that there is no justification, on the basis of health effects alone, to support a standard more stringent than a serious level of 30 p.p.m. for an eight hour period. Dr. Smith suggests, however, that air containing 30 p.p.m. carbon monoxide is nonetheless dirty, and some lower concentration such as 15 p.p.m. is a more desirable measure of air quality.

The assumption here is that air containing 15 p.p.m. carbon monoxide will be clean, or at least cleaner. It is at this point that one departs from considerations of critical levels per se and enters into the more complex business of using carbon monoxide concentrations as an index of overall pollution. The use of carbon monoxide as an index presupposes an exact knowledge of quantitative interrelationships among the various pollutants, as well as a knowledge of the relationship of the index to the sources of pollution. Needless to say, such precise knowledge is lacking.

Despite the fact that urban concentrations of carbon monoxide may be largely derived from vehicle exhaust, other important sources can and do exist, particularly in industrial communities. The contaminants from in-

## CO levels do not follow gas consumption



**Control devices.** Weinstock has compared maximum hourly CO averages during each month for downtown Los Angeles (from data obtained from the California Department of Public Health) with gasoline consumption in that area, and found no correlation. The steep drop in maximum hourly average CO concentrations in 1961-62 is not readily explainable, but the drop in 1966 levels, particularly for the momentary peak values observed each month, mark the advent of control devices which limit CO emissions to 1.5%

dustrial stacks or apartment house incinerators can be quite different from vehicular exhaust. Good correlations of nitric oxide levels with those for carbon monoxide exist; however, such correlation does not always hold with other urban pollutants. For example, levels of carbon monoxide in some urban areas have not correlated well with levels of ozone and total oxidants; total oxidants oftentimes vary inversely with sulfur dioxide and oxides of nitrogen. The breakdown in the validity of a carbon monoxide index might be particularly acute where photochemical reactions occur.

### Health effects

When one speaks about critical levels of carbon monoxide, one should mean critical for reasons of health. We have difficulty with the concept that physiological effects should not be the controlling factors in establishing standards for this gas. If levels are not to be established on the basis of health effects, then what should be the controlling factor?

Faced with lack of information on the physiological effects of low levels of carbon monoxide, one should obtain the necessary information, particularly on the effects of mixtures of pollutants in concentrations actually

found in the environment. There is also a need for accurate information on residence time of carbon monoxide in the lower atmosphere, as well as the mechanism by which it is removed.

Rather than using carbon monoxide levels as an index of pollution and continuing to assign lower permissible concentrations to carbon monoxide in order to hopefully achieve a lowered general pollution level, more effort should be expended in setting standards for carbon monoxide on the basis of the specific effects attributable to this gas. Similarly, the specific effects of other agents, such as sulfur dioxide, oxides of nitrogen, ozone, hydrocarbons, and particulates should be carefully determined, as well as their effects in combination.

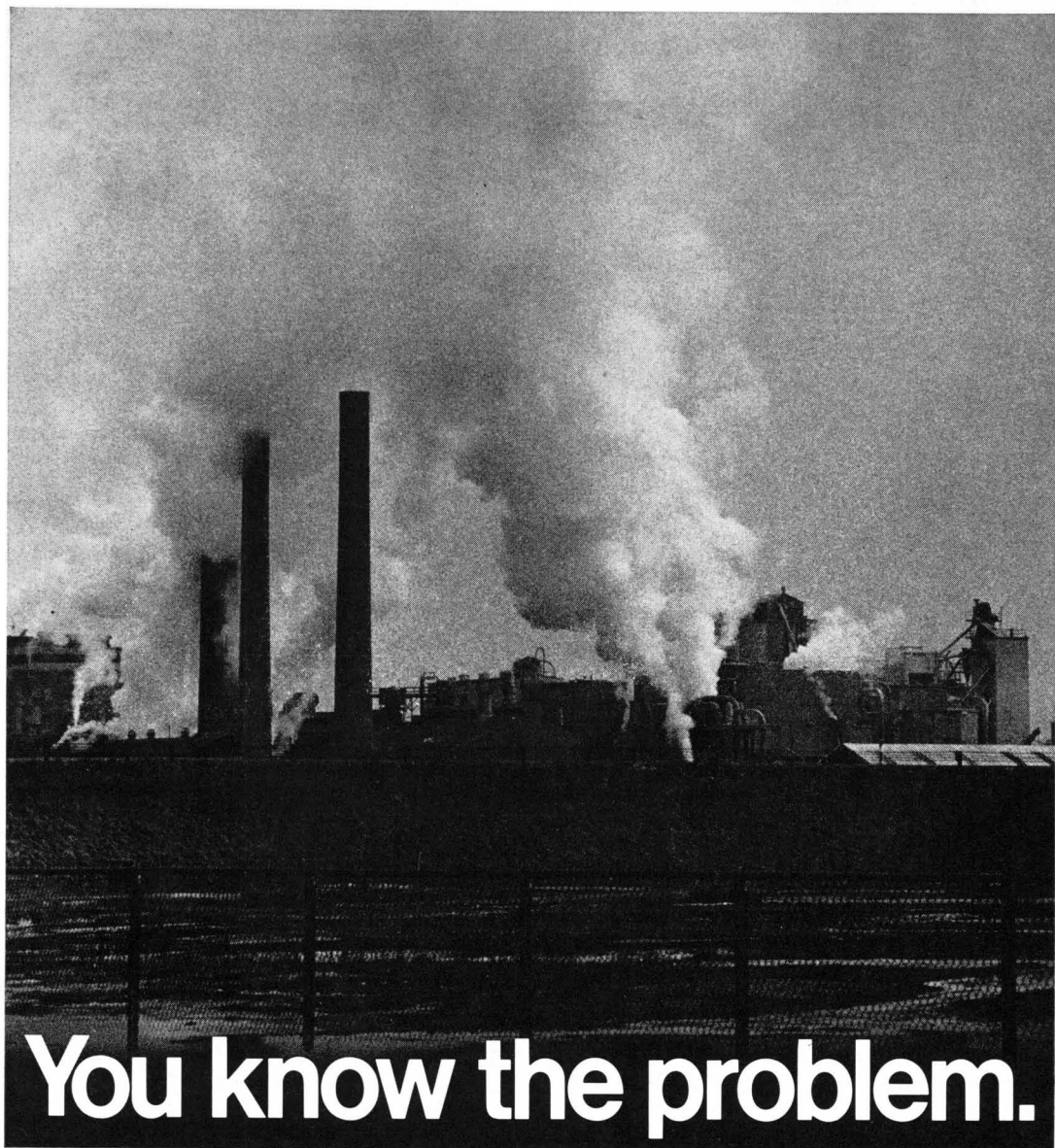
Finally, several indices of overall pollution should be derived: one based on health effects, another on economic factors, another perhaps on aesthetic factors, and so forth. The distinction between air quality criteria based on demonstrable health effects and those having other bases should be vigorously upheld. This in no way impedes progress toward reduced pollution; one can continue to reduce levels to minuscule amounts, but at least the basis upon which the action is taken is clearly identifiable.

**Smith:** As one who is not responsible for the control or reduction of air pollution, I hope that my views are based on a completely objective, albeit imperfect, appraisal of existing data and reasonable extrapolations to what our society demands. It was in this spirit that I expressed the opinion that the California limit of 30 p.p.m. is adequate to protect human health. There are uncertainties about this limit and it would probably be scientifically preferable to set no limit until more research has been done. It may be pertinent that the permissible concentration of CO in space cabins for long missions—100 and 1000 days—has been set at 15 p.p.m., based on 12 hour averages. In this case, the uncertainties of effects at levels higher than 15 p.p.m. have apparently not been considered sufficient to justify levels of CO which could conceivably affect an astronaut's judgment.

My own suggestion that 15 p.p.m. CO might be a more realistic standard was clearly stated to be based on aesthetic considerations, which are certainly debatable. It is debatable in the first place whether my premise is even correct, and I offered some data, and some judgment, to support it.

I still feel certain that urban air pollution of nonspecific origin, measured where I suggested, will commonly consist of a mixture of pollutants, including CO, and that these CO levels will actually represent diluted vehicle exhaust products. The ratio of CO to NO<sub>x</sub>, or to anything else, for that matter, may not be predictable, and the data presented for four years of Detroit sampling are simply an accounting of what was measured. As alterations in exhaust emissions from new cars occur, any such ratios will naturally change, but the rate of change will be slow, and years will be required before drastic changes are seen.

I feel, therefore, that there is no need to adopt CO as an index of urban air pollution, and did not mean to so imply, but it may well be an index whether or not we care to recognize and use it. It seems inherently unsound to permit air to contain a quantity of CO which, though not injurious, can only be achieved when other limits of air purity may be exceeded. It is not necessarily true, however, that I am correct in believing that this situation does or will always obtain, and I sincerely hope that those charged with issuing criteria will test the validity of such an estimate.



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## Aerosol Size Spectrometry with a Ring Slit Confuge

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■ This paper describes the design and the performance of a modified confuge which has an aerosol inlet in the form of a ring slit. The modification was conceived to facilitate high aerosol sampling rates at reasonable size resolutions in terms of aerodynamic diameters. In the size range between  $4 \times 10^{-4}$  and  $1.3 \times 10^{-5}$  cm., the instrument permits sampling rates of 1 liter per minute or more at a size resolution of better than 7%. In any single test run, a size range of about one order of magnitude can be resolved. These results seem to be close to the optimum performance data expected from theoretical considerations. For the size range between  $1.3 \times 10^{-5}$  and  $6 \times 10^{-6}$  cm., the sampling rate fell short of theoretical expectations and had to be reduced to about 0.1 liter per minute in order to give acceptable results. This rate is comparable with maximum sampling rates of other confuge designs. It seems to be an upper limit at high rotor speeds and low linear flow velocities for confuge versions with aerosol entrainment under tangential accelerating forces.

The determination of the particle size distribution of an aerosol is probably the most ambiguous of all basic experimental analyses in aerosol research. The problem exists primarily because the particle size is subject to a special definition whenever the particles are not of homogeneous density and spherical shape. In most experimental cases, spherical particles are the exception rather than the rule and, therefore, "size" has to be defined in some arbitrary way. All special definitions are designed to suit either the experimental method of analysis or the particular purpose of the study. The common denominator of many of these definitions is that the size of a spherical particle will be represented by the actual particle diameter.

For aerosol studies concerning the dynamic properties of particles in the airborne state, the Stokes diameter of a particle is a special definition which is appropriate for many studies in this field and has to be measured in specially designed experimental arrangements. The Stokes diameter of a particle is defined as the diameter of a sphere which would have the same density and, in a mechanical force field, attain the same settling velocity as the particle under consideration. This definition of size is a proper parameter for aerosol particles. It enters a quantity called the relaxation time of an aerosol particle, which plays an important role in the mechanics of aerosols (Fuchs, 1964). For this reason, it is also of

great influence on the deposition pattern and, thus, on the potential health hazard of inhaled aerosol particles consisting of toxic or radioactive material or carrying such components. The correlation to other than aerodynamic properties, however, is less simple. Deriving the mass or the surface area of an irregular particle from its Stokes diameter requires, as for most other size definitions, the knowledge of special particle shape factors which are difficult to obtain (Stoerber, 1965).

The quantitative relation for the Stokes diameter is formally given by

$$D_{st}^2 + 2\beta D_{st} = \frac{18\eta u}{\rho z} \quad (1)$$

where

$$\beta = \alpha_0 \Lambda \quad (2)$$

is a factor representing a first approximation of Cunningham's correction of Stokes' law. For coarse aerosol particles, this term may be neglected, but it becomes significant when the particle size approaches the order of magnitude of the mean free path length of the air molecules. For spherical particles, an empirical value of  $\alpha_0 = 1.246$  is widely accepted.

In most field experiments, the correct Stokes diameter cannot be determined, because the density of the aerosol particle remains unknown and may not be the same for all particles of the aerosol cloud under investigation. In these cases, a kinetic or aerodynamic diameter,  $D_{kin}$ , is defined in formal analogy to the Stokes diameter by

$$D_{kin}^2 + 2\beta D_{kin} = \frac{18\eta u}{\rho_0 z} \quad (3)$$

where we arbitrarily put  $\rho_0 = 1$ . Other names for this definition are "reduced Stokes diameter" or "reduced sedimentation diameter" (Fuchs, 1964). The kinetic diameter also properly describes the aerodynamic behavior of an aerosol particle. However, it does not generally represent the actual diameter of a spherical particle, except in case of a particle of unit density (e.g., water droplets). A comparison with Equation 1 reveals that

$$D_{kin} = \sqrt{\beta^2 + 2\beta \frac{\rho}{\rho_0} D_{st} + \frac{\rho}{\rho_0} D_{st}^2} - \beta \quad (4)$$

Since the aerodynamic size of irregular particles cannot be determined by microscopic measurements, it is generally necessary to separate the airborne particles prior to their deposition in such a way that their aerodynamic size is related

to their location in the collecting device. A common instrument suitable to some degree for this purpose is the cascade impactor (May, 1945; Mercer, 1963). The different impaction stages of this device produce deposits of defined size ranges which can be analyzed separately. If a continuous size spectrum in terms of aerodynamic diameters is desired, it is more advantageous to use an experimental arrangement where a laminar flow of air passes through a transversal mechanical force field which elutriates the particles in the air according to their settling velocity, i.e., kinetic diameter. In the case of dusts and other coarse aerosols where the kinetic diameter is not less than about  $10^{-4}$  cm., the particle separation can easily be effected by the gravitational field acting upon a laminar flow of air passing through a horizontal duct (Polley, 1960; Hemeon, Haines *et al.*, 1961; Timbrell, 1954; Boose, 1962). For smaller particles, however, Brownian motion limits the applicability of gravitational devices (Stöber, 1964). In this case, more powerful force fields, which are technically available with centrifuges, must be applied.

In size-separating centrifugal devices, the air ducts participate in the rotation of the centrifuge rotor in such a way that the air flow is perpendicular, or almost perpendicular, to the centrifugal force field. In this way, the same principle of size separation as in gravitational devices can be applied. There are also the same restrictions. In the duct, a laminar flow of air is required, and the transversal velocity of the particle in the direction of the centrifugal field must be considerably greater than the rate of the particle displacement caused by diffusion.

As in gravitational instruments, two methods of aerosol deposition have been utilized in actual centrifuge designs. One method provides only partial size separation and, in this case, the aerosol enters the duct over the whole cross section. The other method facilitates complete size separation by releasing the aerosol from an inlet nozzle into a laminar flow of clean air.

The first type of centrifuge has the advantage of a relatively high sampling capacity, but suffers from the drawback that the incomplete particle size separation requires tedious mathematical evaluation procedures which give only approximate results for the actual kinetic size distribution of an aerosol deposit. Due to this difficulty, size-related chemical analyses of deposits obtained with this type of centrifuge are of little value. Two models of this design have been described in the literature, a dust centrifuge by Kast (1961) and an aerosol centrifuge by Goetz, Stevenson, *et al.* (1960), which is incorrectly named an aerosol spectrometer.

The other type of centrifuge represents a true particle size spectrometer. Sawyer and Walton (1950), the first authors reporting on such an instrument, called their design a "conifuge." Figure 1 shows the working principle in a schematic diagram. Between the funnel-shaped lid and the inner cone of the rotor, a laminar flow of recycled clean air is drawn down from the top by centrifugal forces. The flow rate in the conical duct is controlled by outlet jets in the rotor base. By withdrawing some air through the aerosol flow valve of the sealed housing of the instrument, an equal amount of aerosol is fed into the duct by a nonrotating inlet nozzle at the tip of the cone. At this point, the particles are entrained in the laminar flow of clean air and become subject to the centrifugal field. Since all particles start from the same location, all trajectories of particles of equal kinetic diameter end at the same annular ring on the inner wall of the funnel-shaped lid, where they can be investigated. For a polydisperse aerosol, the deposition pattern results in a particle size spectrum extending from the top to the base of the cone.

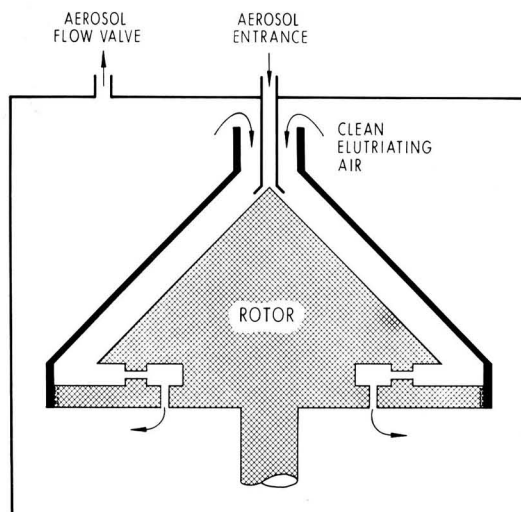


Figure 1. Schematic diagram of the conifuge

The drawback of this design is the relatively low sampling rate. In case of nongaseous atmospheric pollutants, which usually occur at rather low concentrations, the conifuge requires very long sampling times. Apparently for this reason, the original conifuge has been applied only to studies on airborne particles of high concentrations, as they are found in mining operations. The sampling rate was  $25 \text{ cm}^3$  per minute. Modified designs by Keith and Derrick (1960), who used their instrument for studies on cigarette smoke, and by Hauck and Schedling (1968), who improved the flow control system of the instrument, were primarily aimed at extending the lower size limit of deposition. Increasing the speed of these conifuges up to 8000 r.p.m. made it possible to precipitate particles of less than  $10^{-5}$  cm. of kinetic diameter at sampling rates up to  $300 \text{ cm}^3$  per minute.

#### Design of the Ring Slit Conifuge

To facilitate a higher sampling rate without abandoning the principle of complete particle size separation, efforts were made to design centrifugal instruments complying with such requirements (Stöber and Zessack, 1966). Figure 2 shows an assembly drawing of one of these devices which has been built and tested in this laboratory. The model retains some of the essential features of the conifuge, but has been redesigned with regard to the aerosol inlet system, the top section of the clean-air duct and the slope of the cone. The latter modification is actually a compromise between theoretical considerations calling for a cylindrical design and technical difficulties for an extended cylindrical rotor with simple arrangements for an exchangeable sampling foil. Therefore, the conical shape was retained in the lower section of the duct where the aerosol is deposited, but the slope was reduced to an angle of  $20^\circ$  with respect to the axis of rotation.

The aerosol enters the new design through a nonrotating cylindrical duct, 1, and is then led to an adjustable annular slit, 2, where it is entrained by the clean air flowing down the conical section, 3, of the annular duct formed by the cone, 7, and the funnel-shaped lid, 8. On its inside, the lid holds a removable foil which forms the outer wall of the conical section of the duct. Figure 3 shows a photograph of the lid with a black paper foil in place. The clean air enters the conifuge

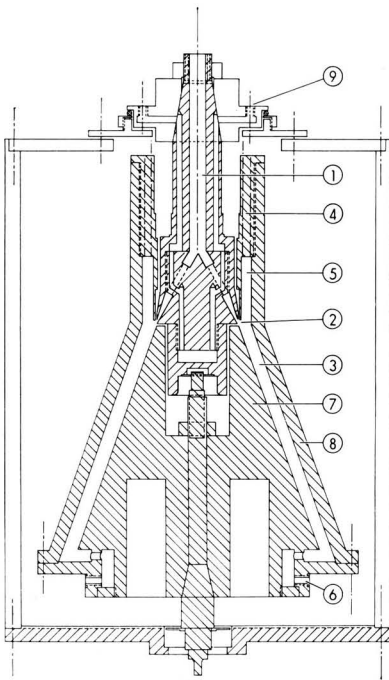


Figure 2. Design of the ring slit confuge (different shading discriminates rotating from nonrotating parts)

fuge at the top of the rotor through an annular arrangement of vertical capillaries, 4, feeding into the cylindrical section of the annular duct, 5. Some of the capillaries are visible from the inside of the lid on Figure 3. The flow in section 5 and 3 is controlled by six equally sized outlet jets, 6, which are located in the base of the cone, 7. The actual arrangement is shown on the photograph of the cone in Figure 4. After

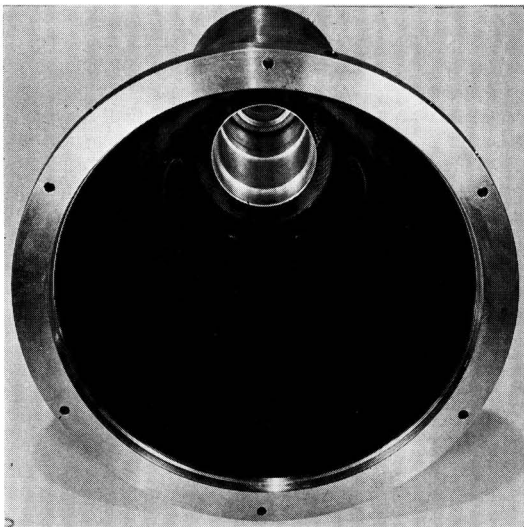


Figure 3. View of the inside of the funnel-shaped lid of the rotor with a black paper foil in place

passing through the jets, the air is recycled inside the housing to the capillaries. Withdrawing a small portion of the circulating air from the sealed housing results in an equal amount of aerosol entering through the slit, 2. The instrument has a cooling duct, 9, to prevent the rotor from warming up by bearing friction. For speeds exceeding 6000 r.p.m., an additional jacket is needed around the outside of the rotor to prevent temperature increases from air friction.

The ring slit inlet for the aerosol was designed to facilitate higher flow rates than permissible for the conventional confuge. This seemed possible for two reasons. First, compared to the narrow aerosol inlet nozzle of the conventional confuge, the ring slit confuge provides a much larger cross-sectional area through which the aerosol enters the conical duct. So, at the same linear velocity of the aerosol flow, the ring slit confuge has a higher flow rate in terms of volume flow. Secondly, at the point of aerosol entrainment of the two designs, the cross-sectional area of the duct is greater for the ring slit confuge than for the original confuge, if the width between the aerosol inlet and the opposite wall is the same. Since both ducts have their minimum cross-sectional area at the aerosol inlet, the Reynolds number for the flow in the duct rises here to a maximum value which, at a given flow rate, will be lower for a ring slit design than for the nozzle arrangement. Accordingly, the ring slit confuge permits a higher flow rate before the critical Reynolds number for unstable flow is approached.

The coaxial capillaries at the top of the rotor serve two purposes: At any flow rate of the clean air, they ensure the angular acceleration of the air to the speed of the rotor, thus providing the condition for proper laminar flow in the annular duct, 5. At the same time, they precipitate residual aerosol particles which may have escaped prior precipitation in the conical section, 3, of the duct because of a size smaller than a critical size defined by the operating conditions.

The rotor lid measures 31.5 cm. from the top to the base. The inside diameter at the base is 21.8 cm. The ring slit inlet for the aerosol has an outer diameter of 6.53 cm. and the radial width of the conical section of the duct is 1.00 cm

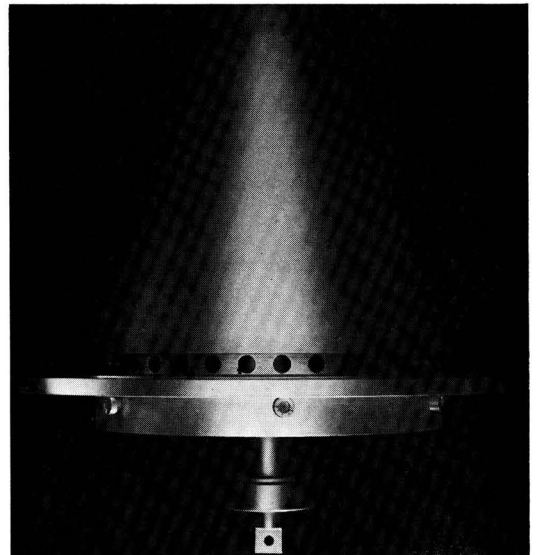


Figure 4. Inner cone of the rotor showing outlet conduit and three outlet jets in the base



The housing is 38.1 cm. high and has an outer diameter of 30.5 cm. The driving motor (Stanley H 260-H, 1.25 HP) is mounted underneath the housing and directly geared to the rotor by a rubber clutch. The instrument can be operated at various motor speeds up to 12,000 r.p.m. and operating conditions utilizing different sets of outlet jets for flow control have been tested at 1500, 3000, 6000, and 9000 r.p.m.

### Theoretical Considerations

An elementary calculation of the particle trajectories and the deposition pattern of particles of different aerodynamic sizes has been made in a previous paper (Stöber and Zessack, 1966). With the designations as shown in Figure 5, an approximate solution for the particle trajectory under initial conditions  $h = H_0 - \delta$ ,  $l = l_a$ , is

$$h = H_0 - \delta + kH_0 [4(l^3 - l_a^3) \sin^2\phi + 3H_0(l^2 - l_a^2) \cos^2\phi \sin\phi] \quad (5)$$

where

$$k = -\frac{\rho_0 \pi^3 N^2 (D_{kin}^2 + 2\beta D_{kin}) \cos\phi}{27\eta F} \quad (6)$$

At  $h = 0$  the trajectory ends on the outer wall of the duct, and with

$$L = l - l_a \quad (7)$$

we obtain from Equations 5, 6, and 7

$$\frac{N^2(D_{kin}^2 + 2\beta D_{kin})}{F} = \frac{54\eta(H_0 - \delta)}{[(4L^2 + 12Ll_a + 12l_a^2) \sin\phi + 3H_0(L + 2l_a) \cos^2\phi] \times \rho_0 \pi^3 H_0 L \sin 2\phi} \quad (8)$$

This equation relates the kinetic size of a particle starting at  $L = 0$  and  $h = H_0 - \delta$  to the location of precipitation,  $L$ , which depends upon the operating conditions, i.e., rotor speed,  $N$ , and total flow rate,  $F$ . Including a term with  $\beta$ ,

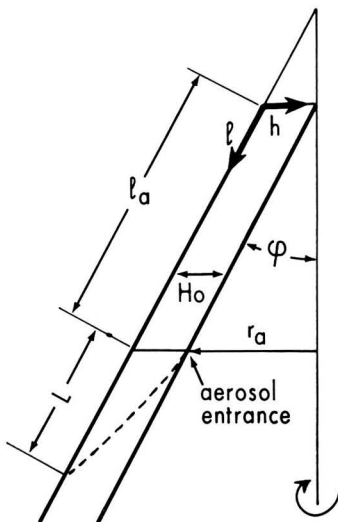


Figure 5. Coordinate system of the conical duct

Equation 8 also accounts for the Cunningham correction, which noticeably improves the agreement between theory and experiment for particles of sizes comparable to the mean free path length of the air molecules (Hauck and Schedling, 1968).

For a given design, the right side of Equation 8 is a function of  $L$  only

$$\frac{N^2(D_{kin}^2 + 2\beta D_{kin})}{F} = f(L) \quad (9)$$

According to the design data, the minimum value of this function, which occurs at  $L = L_{max}$ , is

$$f_{min}(L) = f(L_{max}) = 1.56 \times 10^{-8} \text{ cm}^{-1} \text{ second}^{-1} \quad (10)$$

It predicts a smallest size of aerosol particles which still may be precipitated in the confuge under given operating conditions,  $N$  and  $F$ ,

$$(D_{kin})_{min} = -\beta + \sqrt{\beta^2 + 1.56 \times 10^{-8} \frac{F}{N^2}} \quad (11)$$

Equation 9 also predicts that the efficiency for particle deposition in the confuge does not change if an increase in flow rate,  $F$ , by a factor of  $X^2$  is compensated by an increase of the rotor speed,  $N$ , by a factor of  $X$ . In other words, by doubling the speed of rotation, the flow rate and the aerosol sampling rate can be increased by a factor of 4 without changing the deposition pattern.

For physical reasons, of course, the increase of the flow rate,  $F$ , is limited, because the air stream must remain in the domain of laminar flow. As pointed out in the description of the new instrument, this requirement is adequately met by the design of the ring slit confuge. From the general expression for the Reynolds number,

$$\text{Re} = \frac{F \rho_{air} 4Q}{Q \eta U} = \frac{4F}{\nu U} \quad (12)$$

where in the cylindrical section, 5, of the duct

$$U = 2\pi(2r_a + H_0) \quad (13)$$

we obtain with the dimensions of the instrument

$$\text{Re}_{max} \approx 0.6F \quad (14)$$

Thus, at a flow of 30 liters per minute, we would not exceed  $\text{Re}_{max} \approx 300$ , which indicates a stable laminar flow.

However, there exists a more restrictive condition in the conical part, 3, of the air duct. In this part, the flow has a radial component which, by Coriolis forces, causes a tangential acceleration of the air stream relative to the spinning rotor. This effect does not easily lend itself to a quantitative mathematical treatment, but it can be roughly approximated by using a one-dimensional model.

Disregarding the actual velocity profile of the flow, we define a radius vector,  $R$ , as shown in Figure 6. At the location indicated by  $R$ , the average flow velocity along the cone can be expressed by

$$v_{cone} = \frac{F}{2\pi R H_0 \cos\phi} \quad (15)$$

Accordingly, the radial component of this velocity is

$$\dot{R} = \frac{F \tan\phi}{2\pi R H_0} \quad (16)$$

and since this will hold for  $R = R_0$  at  $t = 0$ , the time when a volume element of the flow enters the conical section of the duct, we obtain by integration

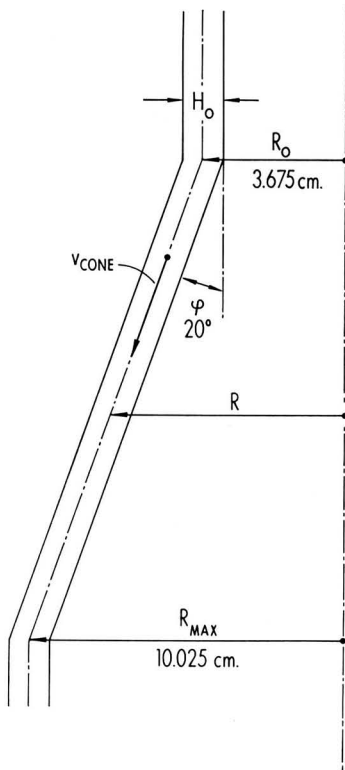


Figure 6. Definition and boundary values of radius vector  $R$

$$R^2 = R_0^2(1 + \alpha Ft) \quad (17)$$

where 
$$\alpha = \frac{\tan \phi}{\pi R_0^2 H_0} = 8.58 \times 10^{-3} \quad (18)$$

The average residence time,  $t_{\max}$ , of a volume element of the flow in the conical duct is

$$t_{\max} = \frac{R_{\max}^2 - R_0^2}{\alpha R_0^2 F} = \frac{751}{F} \quad (19)$$

During this time the volume element, while flowing down the conical duct, is subjected to a Coriolis acceleration

$$b_{\text{cor}} = 2\Omega \dot{R} \quad (20)$$

where

$$\Omega = 2\pi N \quad (21)$$

is the angular velocity of the cone. The Coriolis force causes a tangential velocity component around the cone, which is counteracted by a frictional force originating from the walls of the duct.

For a one-dimensional flow in a plane between two walls (Lamb, 1932) at a distance,  $H_0$ , the average velocity,  $v$ , causes a frictional force per volume element of

$$-\frac{dp}{dx} = \frac{12\eta}{H_0^2} v \quad (22)$$

This is equivalent to a deceleration

$$-b_{\text{fric}} = -\frac{1}{\rho_{\text{air}}} \frac{dp}{dx} = \frac{12\nu}{H_0^2} v \quad (23)$$

and we obtain, in a simplified geometry,

$$\dot{v} = b_{\text{cor}} + b_{\text{fric}} = 2\Omega \dot{R} - \frac{12\nu}{H_0^2} v \quad (24)$$

or

$$R\dot{\omega} = 2\Omega \dot{R} - \frac{12\nu}{H_0^2} R\omega \quad (25)$$

where  $\omega$  is the angular velocity of the flow relative to the cone.

Dividing Equation 25 by  $R$  and utilizing Equation 17, we obtain the differential equation

$$\dot{\omega} = \frac{\alpha\Omega F}{1 + \alpha Ft} - \frac{12\nu}{H_0^2} \omega \quad (26)$$

which has a solution

$$\omega(t) = \alpha\Omega F e^{-\frac{12\nu t}{H_0^2}} \int_0^t \frac{e^{\frac{12\nu \tau}{H_0^2}}}{1 + \alpha F \tau} d\tau \quad (27)$$

describing approximately the angular velocity of a volume element of average flow velocity at time  $t$ , after entering the conical section of the duct.

For various flow rates,  $F$ , and discrete values of  $t \leq t_{\max}$ , limited by Equation 19, a numerical integration of the right side of Equation 27 was made by means of a computer. For any realistic flow rate up to 20 liters per minute, the results indicated that there exists somewhere at  $t \leq t_{\max}$  a shallow maximum for the expression  $R\omega(t)/\Omega$ . For different flow rates, the maxima increase with increasing flow rate in an almost linear manner and reach a value of 3.9 at a flow rate of 20 liters per minute.

These maxima determine the maximum Reynolds number of the tangential flow in the duct because

$$\text{Re} = \frac{R\omega}{\nu} \frac{4Q}{U} = 2 \frac{R\omega}{\nu} H_0 \cos \phi \quad (28)$$

and thus numerically

$$\text{Re}_{\max} = 82.6N \left[ \frac{R\omega}{\Omega} \right]_{\max} \quad (29)$$

This value must remain below the critical Reynolds number for laminar flow conditions, i.e.,

$$\left[ \frac{R\omega}{\Omega} \right]_{\max} \leq \frac{\text{Re}_{\text{crit}}}{82.6N} \quad (30)$$

For a given rotor speed, Equation 30 will put a limit to the flow rate at which the ring slit confuge may be operated.

Although no experimental values for  $\text{Re}_{\text{crit}}$  are available, pertinent Reynolds numbers at which the confuge may be operated safely can be extracted from data given by Keith and Derrick (1960). Their conical duct was designed at  $\phi = 45^\circ$  and  $H_0 = 1$  cm. From their published scale drawing, we can estimate  $0.5 \text{ cm} \leq R_0 \leq 1.5$  cm. The instrument was successfully operated at 8000 r.p.m. and a flow rate of 3.24 liters per minute. Under these conditions, a range of

$$3.5 \leq \left[ \frac{R\omega}{\Omega} \right]_{\max} \leq 5.8 \quad (31)$$

is found with the computer, and the corresponding Reynolds numbers are

$$29,000 \leq \text{Re}_{\text{crit}} \leq 48,000 \quad (32)$$

of which even the lower value exceeds the optimum Reynolds number for laminar flow in a very smooth tube (Dryden,

Murnaghan, *et al.*, 1956) by almost 50%. The reason for this unusual stability may be that for the Keith and Derrick design, in contrast to the situation with the ring slit confuge,  $Re_{max}$  is actually a steep peak around  $L \approx 5$  cm. and, since the formation of turbulence takes some time, it may not develop at all because, with increasing channel length, the flow is rapidly returning to safer values of  $Re$ .

A stabilizing influence due to the density stratification in the centrifugal field may have some effect, although a calculation of the pertinent Richardson number,  $Ri$ , which indicates effective stabilization for  $Ri \geq 1/24$  (Schlichting, 1965) at high Reynolds numbers, gives such values only under favorable conditions and only for a layer approximately described by  $0.3H_0 < h < 0.7H_0$ .

Figure 7 shows the two patterns of Reynolds numbers for the Keith and Derrick confuge. The graph also indicates that the tangential flow in the ring slit confuge is probably in a safe range of Reynolds numbers at a rotor speed of 8000 r.p.m. and a total flow rate of 6 liters per minute. Assuming 15% as the maximum permissible aerosol flow rate, this would facilitate an aerosol sampling rate of up to 0.9 liter per minute, while according to Equation 12 the minimum size collected on the foil would be  $(D_{kin})_{min} = 2.5 \times 10^{-6}$  cm.

At 5000 r.p.m. and a flow rate of 9 liters per minute, the Reynolds number for the tangential flow in the ring slit confuge will remain below the values shown in Figure 7. Thus, it should be possible to sample an aerosol under these conditions at a rate of 22 cm.<sup>3</sup> per second (1.3 liters per minute) with a collectable minimum particle size of  $8 \times 10^{-6}$  cm. This corresponds exactly to the performance data of one channel of the Goetz centrifuge at 24,000 r.p.m. (Stöber and Zessack, 1964). The ring slit confuge design should, then, provide the desired complete particle size separation under conditions which so far have been possible only for devices with a quasicumulative size deposition.

### Experimental

Throughout the performance tests and calibration runs, monodisperse aerosols were used as generated from dilute suspensions ( $\approx 1$  mg. per ml.) of commercially available uniform latex spheres (Dow Chemical Co., Midland, Mich.) by means of an air blast nebulizer. The nebulization rate was about 0.15 ml. per minute. The aerosol output of 8 liters per minute was fed into an open-ended vertical duct. Dry air at a flow rate of 2 liters per minute was added to the duct to facili-

tate evaporation of the original water droplets of the nebulizer. The aerosol was sampled under isobaric conditions from the lower end of the duct. To obtain a heavy, visible deposit in the confuge, the samples were taken over extended periods of time varying between 30 minutes and 2 hours, dependent upon the aerosol flow rate and the concentration in the airborne state. Electrical charges generated on the particles during nebulization had no influence on the particle deposition.

Rotor speeds of 1500, 3000, 6000, and 9000 r.p.m. were selected as standard operating conditions, and different sets of outlet jets consisting of 20-mm. long capillaries of 0.75, 1.50, and 2.00 mm., respectively, and another set with shorter capillaries of 0.33-mm. diameter were used to vary the total flow for a given rotor speed. Since the total flow through the jets could not be determined directly during a run, a number of simulating experiments under static conditions were made, where the flow rate through the rotor was measured under head pressures equal to those theoretically generated by the centrifugal forces in the spinning rotor. The results were taken as approximate values of the actual flow rates by which a reasonable aerosol sampling rate could be selected.

Preliminary tests were then made to determine the optimum values for the width of the ring slit entrance and the ratio of the aerosol flow to the total flow in the simulating experiment. Both parameters, slit width and flow ratio, were correlated so that a higher ratio of aerosol required a wider slit. Aerosol flow rates exceeding 20% of the estimated total flow rate regularly resulted in a less well defined upper edge of the monodisperse deposits on the foil. Thus, a medium slit width of approximately 0.5 mm. (total channel width  $H_0 = 10$  mm.) and an aerosol flow rate of 10 to 15% of the estimated total flow rate were selected for the majority of the tests. This seemed to be a reasonable compromise between resolving power requiring a minimum slit width and sampling efficiency requiring a maximum aerosol flow rate. The final performance tests and calibrations were then conducted under standard operating conditions with various outlet jets and latex particles of sizes between  $2.68 \times 10^{-4}$  and  $8.8 \times 10^{-6}$  cm. diameter. The particles were precipitated in visible quantities on inserted black paper foils. Some of the deposits were investigated by means of a scanning electron microscope. In these cases, the deposits and the foil were coated under vacuum with a thin film of gold. The deposits of the smallest sizes were inspected with a regular electron microscope. For this purpose, Formvar-covered carrier grids were placed in depressions on the paper foil along the channel length in distances of 10 mm. and the grids were inspected after the aerosol had been sampled.

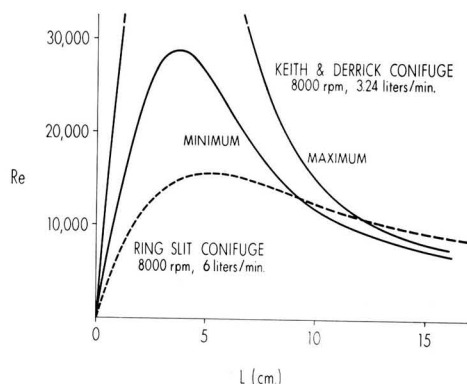


Figure 7. Patterns of Reynolds numbers for tangential flow along the conical duct of the Keith and Derrick confuge and corresponding pattern of the ring slit confuge under presumably safe operating conditions

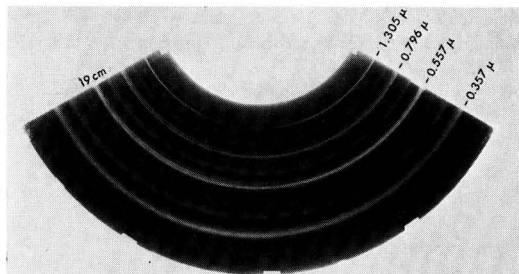


Figure 8. Sampling foil of the ring slit confuge with deposits of monodisperse latex spheres of different size

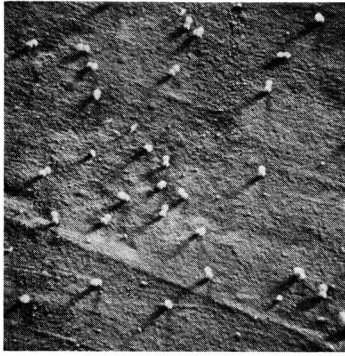


Figure 9. Doublet aggregates of  $3.57 \times 10^{-5}$  cm. latex spheres

### Results

A typical deposit pattern obtained during the performance tests of the ring slit confuge is given in Figure 8. It shows a photograph of a paper foil used in a series of tests with four different latex aerosols at 3000 r.p.m. with 1.5-mm. outlet jets. Under these conditions, a total flow of 7.5 liters per minute was measured in the simulating static experiment. Accordingly, the aerosol sampling rate was set at 1.2 liters per minute and the latex aerosols were sampled, one at a time, for 60 minutes. As a result, a system of easily visible concentric rings was obtained.

Owing to the different sizes, the circular deposits showed different colors of scattered light for any given angle of observation. For each aerosol, there were up to three circles discernible on the foil, a dense circular deposit and additional inner circles of decreasing deposit density. Checking the circular deposits of the coarser particles ( $1.305 \times 10^{-4}$  and  $7.96 \times 10^{-5}$  cm.) under a microscope equipped with a Leitz Ultrapak system verified the assumption that the less intense deposits consisted of aggregates of two and three spheres, respectively. For the smaller latex sizes, micrographs obtained with a scanning electron microscope gave the same results. Figure 9 shows a deposit of doublet aggregates of



Figure 10. Triplet aggregates of  $3.57 \times 10^{-5}$  cm. latex spheres and Figure 10 shows some triangular triplet aggregates of the same aerosol.

With the results of a recent investigation (Stöber, Berner, *et al.*, 1969), all deposits of aggregates could be used in the calibration procedure by applying the appropriate shape factors for aggregates of uniform spheres, i.e., 1.18 for doublets, 1.33 for triplets, and 1.46 for quadruplets. Since the concentration of the latex particles in the nebulizer reservoir was limited to about 1 mg. per ml., no bigger aggregates were produced in the performance tests, except for sizes below  $2 \times 10^{-5}$  cm. For the small latex sizes, the reservoir concentration had to be reduced to about 0.1 mg. per ml. to avoid clusters and obtain single airborne latex spheres.

By using the size data of the aerosol particles and the experimental deposit location,  $L$ , on the foil, Equation 8 was repeatedly solved for the total flow rate,  $F$ , which should not vary at a given operating condition, regardless of the set of

Table I. Determination of Total Flow Rate,  $F$ , at Rotor Speed of 3,000 r.p.m. with 0.75-mm. Outlet Jets by Applying Equation 9 to Experimental Results

Latex Size $\times 10^{-4}$ Cm.	$D_{kin}$ , $\times 10^{-4}$ Cm.	$\sqrt{D_{kin}(D_{kin} + 2\beta)}$ , $\times 10^{-4}$ Cm.	$L$ , Cm.	$\sqrt{f(L)}$ , $\times 10^{-4}$ , (Cm. Sec.) $^{-1/2}$	$F$ , Liters/Min.
Doublet 0.126	0.149	0.216	14.30	1.65	2.57
0.176	0.176	0.245	12.20	1.91	2.47
Doublet 0.176	0.208	0.278	10.70	2.15	2.51
Triplet 0.176	0.234	0.305	9.40	2.40	2.42
0.264	0.264	0.336	8.60	2.60	2.51
Doublet 0.264	0.312	0.385	7.40	2.92	2.61
0.357	0.357	0.431	6.25	3.31	2.54
Doublet 0.357	0.421	0.496	5.25	3.80	2.56
0.557	0.557	0.634	3.45	5.08	2.34
Doublet 0.557	0.657	0.734	2.85	5.70	2.49
0.796	0.796	0.874	2.10	6.98	2.35
1.305	1.305	1.385	0.68	13.00	1.70

**Table II. Average Flow Rates as Obtained by Solving Equation 9, Aerosol Flow Rates, Deposit Patterns, and Maximum Reynolds Number of Tangential Flow under Different Operating Conditions**

Rotor Speed, R.P.M.	Outlet Jets, Mm. Diam.	Av. Flow Rate Liters/Min.	Std. Error, %	Aerosol Flow Rate, Liters/Min.	Deposit Pattern	Re <sub>max</sub>
1500*	2.0	8.3	4.2	0.50	Regular	3820
1500	1.5	5.2	3.2	0.35	Regular	2910
3000	2.0	23	4.1	1.20	Diffusive	17840
					for L > 14 cm.	
3000*	1.5	10.0	2.7	1.20	Regular	8800
3000	1.0	4.3	2.0	0.40	Regular	4340
3000	0.75	2.4	2.9	0.20	Regular	2560
6000	2.0	46	3.2	4.00	Diffusive	50000
					for L > 8 cm.	
6000	1.5	24	4.1	2.00	Diffusive	37200
					for L > 10 cm.	
6000*	1.0	9.7	2.6	1.00	Regular	17590
6000	0.75	7.4	4.2	0.60	Regular	14040
6000*	0.33	3.2	5.0	0.100	Regular	6530
9000	0.75	14	9.9	1.20	Diffusive	35800
					for L > 7 cm.	
9000	0.33	6	—	0.100	Convective turbulence	17440
		(estim.)				

\* Routine operating conditions

particle data inserted. Table I gives a typical result. The flow rate,  $F$ , remains rather constant. The average value is about 20% higher than the flow rate in the simulating static experiment. At 3000 r.p.m. and with 0.75-mm. outlet jets, the mean flow rate obtained from 12 independent measurements utilizing different particle sizes is 2.42 liters per minute, while the standard error is 2.9%.

Experiments under different operating conditions gave similar results. They indicated a regular pattern of flow rate values ranging slightly above average for medium distances,  $L$ , and remaining slightly below average near  $L_{max}$  and at short distances,  $L$ . This pattern reflects the imperfections of Equation 8 due to the simplifications made during its derivation. In general, however, the standard error remained well below 5%. Thus, Equation 8 proved to be a reasonable approximation. The flow rates obtained from it were consistently higher than the ones measured in the simulating experiments under static conditions. This seemed to indicate that the latter ones involved a systematic error. With this somewhat arbitrary assumption, preference was given to the average values computed by Equation 8. That seemed to be justified in view of the fact that for a confuge designed by Tillery (1967), which permits the direct measurement of the total flow rate, Equation 8 gave the correct value within a margin of error of 6% (Moss, 1968).

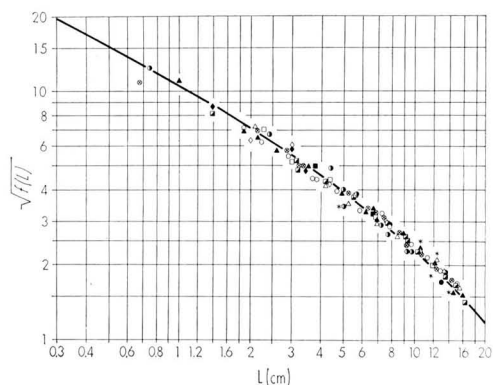
As a consequence of this, all experimental results obtained under different operating conditions could be plotted along a single theoretical curve by using the respective average flow rates as listed in Table II. Figure 11 shows the graph with all the particle data. Due to the logarithmic scales of the coordinates, the small systematic deviations are inconspicuous and largely concealed by the scatter of data from different operating conditions covering the same size range.

As indicated in Table II, not all operating conditions provided a regular deposition pattern over the whole length of the conical duct. At flow rates exceeding 10 liters per minute, the narrow concentric rings of the regular deposition of monodisperse aerosols were generally confined to an area extending from the aerosol entrance to a critical value of  $L$ , beyond which a diffusive deposition with poorly defined

downstream boundary prevailed. This critical channel length,  $L_{crit}$ , decreased when the flow rate or the rotor speed was increased. The sixth column in Table II gives the approximate numerical values for several operating conditions.

Figure 12 is a photograph of a deposition pattern which makes the critical channel length visible. The deposit was obtained in an experiment with  $3.57 \times 10^{-5}$  cm. latex particles at 6000 r.p.m. by employing 1.5-mm. outlet jets. The average flow rate as obtained by Equation 8 was 24 liters per minute. While the doublet aggregates are still deposited on a concentric ring at  $L = 8.6$  cm., the single particles expected to form a circular deposit at  $L = 10.9$  cm., are spread over a large area at  $L \geq 10$  cm. Apparently, this particular operating condition produced a critical value of  $L_{crit} \approx 10$  cm.

The diffusive patterns are, undoubtedly, a result of an ex-



**Figure 11. Theoretical curve and experimental results for particle deposition patterns under various operating conditions**

Operating Conditions:

- 1500 r.p.m., 2.0-mm. outlet jets
- \* 1500 r.p.m., 1.5-mm. outlet jets
- △ 3000 r.p.m., 2.0-mm. outlet jets
- 3000 r.p.m., 1.5-mm. outlet jets
- ▣ 3000 r.p.m., 1.0-mm. outlet jets
- ⊙ 3000 r.p.m., 0.75-mm. outlet jets
- 6000 r.p.m., 2.0-mm. outlet jets
- 6000 r.p.m., 1.5-mm. outlet jets
- ▲ 6000 r.p.m., 1.0-mm. outlet jets
- △ 6000 r.p.m., 0.75-mm. outlet jets
- ◆ 6000 r.p.m., 0.33-mm. outlet jets
- ◇ 9000 r.p.m., 0.75-mm. outlet jets

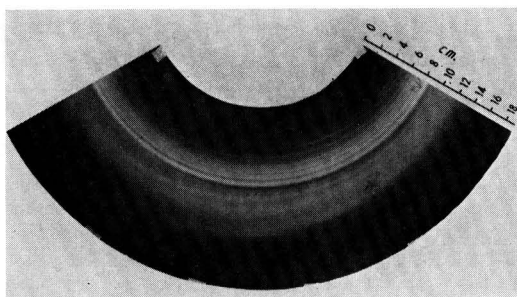


Figure 12. Sampling foil with irregular deposit of  $3.57 \times 10^{-5}$  cm. latex spheres

cessive tangential acceleration of the air flow in the conical duct, as discussed earlier. The critical channel length occurs where the tangential motion has exceeded the critical Reynolds number and becomes turbulent.

Besides this predictable disturbance, another irregularity of the deposition pattern was quite frequently observed at the upper edge of the foil at short values of  $L$ . Deposits in this area were often no longer circular, but consisted of a sequence of turns of a narrow spiral. The effect was more pronounced at high rotor speeds and at increased ratios of aerosol flow rate to total flow rate. A trace of this pattern can be seen in Figure 8, where all circular deposits, except the ones related to  $3.57 \times 10^{-5}$  cm. latex particles, have a substructure with spiral features. Due to this distortion, the particle concentration is not constant along the circular deposit, and there is also a variation in the width of the deposit. The precipitate of the  $1.305 \times 10^{-4}$  cm. particles in Figure 8 shows this effect quite clearly.

Distortions of this kind were caused by a slight eccentricity between the rotating and the nonrotating parts of the aerosol entrance slit, which seems to be extremely sensitive to minute misalignments.

Another difficulty was encountered at high rotor speeds and relatively low flow rates, i.e., with 0.33-mm. outlet jets at 6000 and 9000 r.p.m. Under these conditions, the width of the ring slit had to be narrowed down to about 0.2 mm. and, accordingly, the aerosol flow rate had to be reduced to less than 0.2 liter per minute in order to avoid a disturbance which seemed to produce a convective turbulence. This distortion is probably caused by the relatively low axial flow rate and the enhanced shear at high rotor speeds between the clean air spinning with the rotor and the nonrotating aerosol being entrained into the clean air. It was particularly difficult to avoid this effect at 9000 r.p.m.

In view of the disturbances under some of the operating conditions and in consideration of the similarity of the deposition patterns under some others, the authors selected four particular conditions, as indicated by asterisks in Table II, for the routine operation of the instrument. Figure 13 shows the corresponding calibration curves. They each provide a reasonable size resolution within a size range of about one order of magnitude, and the total range of aerodynamic sizes covered by the four curves reaches from around  $10^{-8}$  cm. to about  $6 \times 10^{-6}$  cm.

Under the four routine conditions, the actual size resolution,  $\Delta D/D$ , was almost constant and remained below 7%. Figure 8 gives a visual indication. According to recent measurements (Stöber, Berner, *et al.*, 1969), the aerodynamic size of triplet aggregates of  $5.57 \times 10^{-6}$  cm. latex spheres is  $7.41 \times 10^{-5}$  cm. The deposit of such triplets in Figure 8 is well separated from the deposit of single latex spheres of  $7.96 \times 10^{-6}$  cm.

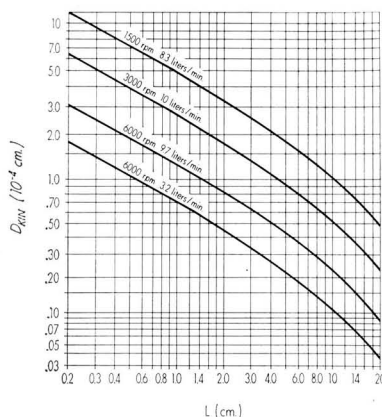


Figure 13. Calibration curves for particle deposition patterns under routine operating conditions

diameter, which indicates a size resolution of better than 7%. With this resolution, a size analysis in the range between  $4 \times 10^{-4}$  and  $1.3 \times 10^{-5}$  cm. permits aerosol sampling rates of 1 liter per minute or slightly more. The separation of smaller sizes down to  $6 \times 10^{-6}$  cm. requires a reduced aerosol flow rate of about 0.1 liter per minute.

#### Discussion

The experimental results indicate that the performance of the ring slit confuge is reasonably close to theoretical expectations.

The deposition patterns are generally in good agreement with Equation 8, which has been proved useful in representing the size deposition of other confuges (Hauck and Schedling, 1968). The equation permits an indirect experimental determination of the total flow rate in the confuge, which value cannot be measured directly.

The stability of the laminar flow in the conical duct as influenced by Coriolis forces is slightly better than the conservative estimate plotted in Figure 7. However, the indication of instabilities observed in an earlier report (Stöber, 1964) turned out to be substantial and, as expected, the stability of the flow did not persist up to the high values of  $Re_{max}$  as computed from the data of Keith and Derrick (1960). The results listed in Table II indicate an unstable flow in the ring slit confuge for  $Re_{max} > 17,600$ .

This value, although unusually high when compared with critical Reynolds numbers for stable flow in other geometric arrangements, was consistent throughout the tests. Possibly, the high numerical values of these Reynolds numbers are due to the one-dimensional approximation of the tangential flow velocities and the fact that the tangential flow takes place in an accelerated system.

The aerosol flow rates of the routine conditions as listed in Table II are values which provide a size resolution of at least 7%. Except for the tests in the range of smallest sizes, i.e., at 6000 r.p.m. and 3.2 liters per minute, the listed aerosol flow rates do not represent the permissible maximum values, but were arbitrarily set at 15% of the estimated total flow rates. Since these estimates were too low, the aerosol flow rate turned out to be only about 10% of the actual flow rate in the instrument. An increase to the anticipated value of 15% will be possible without a significant loss in size resolution.

For high speeds and low flow rates, however, the aerosol flow had to be reduced below the expected ratio. Thus, for aerosol size separations below about  $1.3 \times 10^{-5}$  cm., the

aerosol sampling rate of the ring slit confuge is restricted to about 0.1 liter per minute. This is considerably less than anticipated. The limitation is due to the difficulties encountered at high speed operation, where the coaxial flow velocities are relatively low compared to the relative angular velocities between the clean air and the aerosol. For the same reason, the performance of the instrument at 9000 r.p.m. was not good enough to warrant routine operation at that speed.

A recently completed new design by Hochrainer and Brown (1969) seems to avoid this difficulty by using a ring slit entrance which is part of the rotor and accelerates the aerosol to the proper angular velocity in a radial plane before it enters the conical duct. This rotating slit arrangement, first employed by Berner (1968), provides an excellent size resolution, but sampling rates, so far, were only around 0.02 liter per minute or less. Only for size-separative sampling below sizes of  $1.3 \times 10^{-5}$  cm., may these rates become competitive with our design. Thus, the rotating slit may be a more effective feature in confuges for sampling in the  $10^{-6}$ -cm. size range, particularly if a cylindrical version avoiding Coriolis effects is used and the entrance losses of the aerosol can be controlled.

The formal size distribution analysis of the concentric deposits on the foil is straightforward. We obtain for the frequency of all sizes within  $D \pm \Delta D/2$  the expression

$$\Delta N_p = \frac{\Delta N_p}{\Delta D} \Delta D = -2\pi(L + l_a)C_f \sin\phi \Delta L \quad (33a)$$

which simply indicates that the number of particles in the interval  $\Delta D$ , is proportional to the concentration of the particles on the foil and the area defined by the length of the arc of the deposit and the interval,  $\Delta L$ . In case of a mass concentration,  $C_m$ , on the foil, we obtain a corresponding mass frequency

$$\Delta M = \frac{\Delta M}{\Delta D} \Delta D = -2\pi(L + l_a)C_m \sin\phi \Delta L \quad (33b)$$

Thus, the size distribution function is

$$\frac{dN_p}{dD} = -2\pi(L + l_a)C_f \sin\phi \frac{dL}{dD} \quad (34)$$

where  $dN_p$  and  $C_f$  may be substituted by  $dM$  and  $C_m$ , respectively, when the mass distribution is under consideration. The derivative,  $dL/dD$ , can be obtained from Equation 8 as

$$\frac{dL}{dD} = \frac{18\eta F(D + \beta)H_0}{N^2(D^2 + 2\beta D)^2 \pi^2 (H_0 - \delta)(L + l_a)[2(L + l_a) \sin\phi + H_0 \cos^2\phi] \sin 2\phi} \quad (35)$$

Inserting this into Equation 34 gives

$$\frac{dN_p}{dD} = \frac{18\eta FH_0}{N^2 \pi^2 (H_0 - \delta) \cos\phi} \times \frac{C_f}{D^2 \left( D + 3\beta + \frac{\beta^2}{D + \beta} \right) [2(L + l_a) \sin\phi + H_0 \cos^2\phi]} \quad (36)$$

and there exists a corresponding expression with  $dM$  and  $C_m$  for the mass distribution. For a given operating condition, Equation 8 gives a unique relationship between  $D$  and  $L$ . Thus, for the same conditions, Equation 36 is a function of  $L$  and  $C_f$  only. The distribution analysis would require the

measurement of the foil concentrations along a radius vector,  $L$ , on the foil.

In practice, however, this procedure is only feasible under favorable circumstances. Equation 36 implies a perfect symmetry of the deposits, which is, in the authors' experience, the exception rather than the rule. Depending upon the operating conditions, the unavoidable misalignments, though small, always cause a certain degree of asymmetry. This impairs in many cases the evaluation of the deposit by means of Equation 36, because the concentration along a concentric arc is not constant. Empirical correction factors for selected locations are impractical in view of the fact that slight changes of the misalignment of the entrance slit cause significant shifts of the asymmetrical pattern. Hence, it is necessary to integrate the foil concentration along concentric arcs.

For a number frequency determination, such a procedure involves a disproportionate amount of microscopic work, which is prohibitive for most practical purposes. A mass distribution analysis, however, is feasible, provided that the precipitated quantities are sufficiently large and can be subjected to a quantitative physical, chemical, or radiographic mass analysis. In this case, the paper foil with the deposit may be cut into annular sections of width  $\Delta L$ , which then can be analyzed separately. With the mass,  $M_L$ , on an annular strip, the mass distribution function is simply approximated by

$$\frac{dM}{dD} = \frac{M_L}{\Delta L} \frac{dL}{dD} = \frac{M_L}{\Delta D} \quad (37)$$

where the representative value of  $D$  may be taken at the middle of the interval  $\Delta D$ , as obtainable from  $\Delta L = L_2 - L_1$  and the calibration curve.

For the routine operating conditions of the present design, adequate information can be collected if the width  $\Delta L$  of the annular strips is varied so that approximately

$$\Delta L \approx 0.1L \quad (38)$$

This is equivalent to

$$\Delta \log L \approx 0.043 \quad (39)$$

and it can be seen from the calibration curves that there are corresponding intervals

$$\Delta \log D \approx 0.043 \quad (40)$$

or

$$\frac{\Delta D}{D} \approx 0.1 \quad (41)$$

which is adequate in view of the actual resolution of the instrument. Furthermore, these relationships suggest that the most pertinent way of presenting the mass distribution data obtained by the procedure just described would be in terms of a logarithmic distribution function

$$\frac{dM}{d \log D} = \frac{DM_L}{\Delta D} \times \frac{1}{\log e} \quad (42)$$

By selecting proper interval limits,  $L$ , close to Equation 38, this relation facilitates an equidistant data presentation which makes optimum use of the actual size resolution. Between  $L = 1$  cm. and  $L = 16$  cm., there may be as many as 25 annular sections which provide mass distribution data at a size resolution of about 10% over a size range of almost one order of magnitude. In addition, the innermost strip will give cumulative information on the mass of all coarser particles.

While the possibility of a simpler deposit evaluation of

conifuges by means of Equation 36 may be a matter of mechanical precision and skill during the construction of the instrument, it seems to be practically impossible to maintain in any conifuge design a size dispersion along  $L$  in the conical or cylindrical duct, which for a single test run would permit a practical size resolution of better than 10% over a size range of more than about one order of magnitude at aerosol flow rates of 1 liter per minute or more.

Thus, except for the size range below  $1.3 \times 10^{-5}$  cm., the ring slit conifuge as described here is performing rather close to the optimum efficiency which a conifuge design can possibly achieve.

#### Acknowledgment

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#### Nomenclature

- $\alpha$  =  $8.578 \times 10^{-3}$  cm.<sup>-3</sup> (Equation 18)  
 $\alpha_0$  = 1.246; empirical factor  
 $\beta$  =  $8.2 \times 10^{-6}$  cm. (Equation 2)  
 $\delta$  = coordinate of aerosol inlet, parallel to  $h$ , cm.;  $\delta \ll H_0$   
 $\eta$  =  $1.83 \times 10^{-4}$  gram cm.<sup>-1</sup> sec.<sup>-1</sup> at 20° C.; viscosity coefficient  
 $\phi$  = 20°; semiangle at apex of cone  
 $\nu$  = 0.143 cm.<sup>2</sup> sec.<sup>-1</sup>; kinematic viscosity coefficient  $\frac{\eta}{\rho_{\text{air}}}$   
 $\Lambda$  =  $6.53 \times 10^{-6}$  cm.; mean free molecular path length  
 $\rho$  = particle density, gram cm.<sup>-3</sup>  
 $\rho_0$  = 1 gram cm.<sup>-3</sup>; unit density  
 $\rho_{\text{air}}$  =  $1.29 \times 10^{-3}$  gram cm.<sup>-3</sup>; density of air at room temperature  
 $\omega$  = angular velocity of air flow relative to the cone, sec.<sup>-1</sup>  
 $\Omega$  = angular velocity of the cone, sec.<sup>-1</sup> (Equation 20)  
 $\Delta D/D$  = relative size resolution  
 $b_{\text{cor}}$  = Coriolis acceleration, cm. sec.<sup>-2</sup>  
 $b_{\text{fric}}$  = frictional acceleration, cm. sec.<sup>-2</sup>  
 $C_f$  = number concentration of particles on the foil, cm.<sup>-2</sup>  
 $C_m$  = mass concentration of particles on the foil, gram cm.<sup>-2</sup>  
 $\left. \begin{matrix} D_{\text{kin}} \\ D \end{matrix} \right\}$  = aerodynamic diameter, cm.  
 $D_{\text{st}}$  = Stokes diameter, cm.  
 $F$  = total volume flow rate, cm.<sup>3</sup> sec.<sup>-1</sup>  
 $h$  = coordinate of radial width of conical duct, cm.  
 $H_0$  = 1.000 cm.; radial width of conical duct  
 $l$  = distance of a location on the conical wall from apex, cm. (Figure 5)  
 $l_a$  = 9.283 cm.; distance of aerosol inlet from apex of cone (Figure 5)  
 $L$  =  $l - l_a$  (Figure 5 and Equation 7)  
 $L_{\text{max}}$  = 16.3 cm.; maximum coordinate of channel length with evaluable deposit  
 $L_{\text{crit}}$  = critical coordinate of channel length beyond which diffusive deposition occurs, cm.  
 $M$  = total mass of deposited particles on the foil, grams  
 $M_L$  = mass of all particles deposited on annular strip of width  $\Delta L$ , gram.  
 $N$  = rotor speed, sec.<sup>-1</sup>  
 $N_p$  = total number of deposited particles on the foil

- $p$  = air pressure, dyne cm.<sup>-2</sup>  
 $Q$  = cross-sectional area, cm.<sup>2</sup>  
 $r_a$  = 3.175 cm.; distance of aerosol inlet from axis of rotation  
 $R$  = radius vector of center of conical duct (Figure 6)  
 $R_0$  = 3.675 cm.; radius vector of center of conical duct at aerosol inlet (Figure 6)  
 $\dot{R}$  = derivative of  $R$  in time, cm. sec.<sup>-1</sup>  
 $R_{\text{max}}$  = 10.025 cm.; radius vector of center of conical duct at end of cone (Figure 6)  
 $Re$  = Reynolds number  
 $Re_{\text{max}}$  = maximum Reynolds number for tangential flow  
 $Re_{\text{crit}}$  = critical Reynolds number for stable flow  
 $Ri$  = Richardson number  
 $t$  = time after volume element of flow entered conical duct, sec.  
 $t_{\text{max}}$  = maximum residence time for volume element of average flow rate, sec.  
 $u$  = steady-state settling velocity, cm. sec.<sup>-1</sup>  
 $U$  = circumference of a duct, cm.  
 $v$  = linear flow velocity, cm. sec.<sup>-1</sup>  
 $\dot{v}$  = derivative of  $v$  in time, cm. sec.<sup>-2</sup>  
 $z$  = mass acceleration, cm. sec.<sup>-2</sup>

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# Absolute Calibration of a Flame Photometric Detector to Volatile Sulfur Compounds at Sub-Part-Per-Million Levels

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■ Permeation tubes were used to obtain an absolute calibration of a flame photometric detector (FPD) to sulfur dioxide, hydrogen sulfide, methyl mercaptan, and carbon disulfide. Response data was obtained from 0.001 to 10 p.p.m. for each compound. Preliminary experiments with the FPD as an ambient air sulfur dioxide monitor indicated that the detector has potential utility as a continuous monitoring device.

Brody and Chaney (1966) described the development of a hydrogen-air flame photometric detector (FPD) system designed to produce a semispecific linear response for volatile phosphorus and sulfur compounds. Crider (1965) also described the use of a flame photometric detector for the monitoring of atmospheric sulfur dioxide and sulfuric acid aerosols. Crider's apparatus required large volumes of hydrogen and air to achieve sub-part-per-million detection levels, and the system's response to SO<sub>2</sub> was approximately linear between 0.3 and 1.2 p.p.m.

The system designed by Brody and Chaney was arranged with a photomultiplier tube viewing a region above the flame through narrow-band optical filters. Sulfur compounds, when introduced into the hydrogen-rich flame, produced strong luminescent emissions between 300 and 425 m $\mu$ . By use of a narrow-band optical filter that permitted maximum transmission at 394 m $\mu$ , a 30,000 to 1 specificity ratio of sulfur to nonsulfur compounds was achieved with the exception of phosphorus compounds when the specificity was about 10,000 to 1.

Stevens (1967) described some of the difficulties experienced in determining response characteristics of the same flame photometric detector to sulfur dioxide, hydrogen sulfide, methyl mercaptan, and carbonyl sulfide. Stevens' approach was one of continuous introduction of the contents of an exponential dilution flask into the carrier gas entering the detector. This preliminary study indicated that levels as low as 0.05 p.p.m. could be detected. Because of the sorption of the sulfur gases on the walls of the flask, difficulty was encountered in demonstrating response at lower levels. Attempts to introduce sulfur dioxide at levels below 1 p.p.m. into a gas chromatograph and to detect the eluents from the column with the FPD were unsuccessful, mainly because of the interaction of sulfur dioxide with the active sites of the gas chromatographic system.

O'Keeffe and Ortman (1966) described the development of the permeation tube as a primary standard source. They showed that a liquefiable gas such as sulfur dioxide, when enclosed in an inert plastic tube, escapes at a constant reproducible temperature-dependent rate, and can thus serve as a primary standard for the calibration of air pollution analyzers.

In order for the Public Health Service's National Air Pollution Control Administration to determine effects of sulfur dioxide on man, animals, vegetation, and materials, an accurate value for the hourly, daily, and annual SO<sub>2</sub> concentration in several urban locations must be obtained.

Current air monitoring instruments are based on conductimetric, colorimetric, or coulometric principles. These instruments require daily attention, are subject to interferences from ambient concentrations of nonsulfur pollutants, and are marginal in sensitivity with regard to detection below 0.03 p.p.m. The flame photometric detector herein described could, with certain modifications, serve as a reliable, sensitive, continuous SO<sub>2</sub> ambient air monitor. This report describes the use of permeation tubes to characterize the response of the flame photometric detector to sub-part-per-million levels of sulfur dioxide, carbon disulfide, methyl mercaptan, and hydrogen sulfide in air.

## Experimental

A Melpar, Inc. (Falls Church, Va.) flame photometric detector and a Micro-Tek Instruments, Inc. (Baton Rouge, La.) electrometer and power supply were used to obtain the data reported here.

Operating parameters of the FPD were as follows:

Air Flow	= 180 ml. per minute
Hydrogen Flow	= 200 ml. per minute
Detector Temperature	= 120° C.
Phototube Voltage	= 750 volts DC

The narrow band optical interference filter used in this study had a maximum transmittance of 67% at 394 m $\mu$  and a half-band width of 5 m $\mu$ .

Permeation tubes were prepared as described by O'Keeffe and Ortman (1966) and calibrated gravimetrically at 20.3° C.

**Permeation Tube Calibration.** Hydrogen sulfide and methyl mercaptan tubes were protected from air oxidation, except when being used for generating air mixtures, by passing a slow stream of nitrogen over them. The tubes were weighed periodically over 6 weeks to determine their rates of weight loss. Table I lists the weight and volume loss characteristics found for each tube. From this calibration study, the graph in Figure 1 was prepared. The graph was plotted by assuming that the materials to be studied would behave as ideal gases at the levels of interest. From this assumption the following equation permits calculating parts-per-million (V./V.) permeand as a function of air flow rate over the tube.

$$C = \frac{Pr}{M} \times \frac{G}{L}$$

Table I. Permeation Tube Output Characteristics

Sample	Weight Loss, $\mu\text{g}/\text{Min. at}$ 20.3° C.	Relative Standard Error <sup>a</sup>	Volume Loss, $\mu\text{l}/\text{Min. at}$ 20.3° C. at 1 Atm.
H <sub>2</sub> S	0.183	±4.0%	0.120
SO <sub>2</sub>	1.040	±1.7%	0.364
CS <sub>2</sub>	1.279	±2.3%	0.377
CH <sub>3</sub> SH	0.187	±3.5%	0.087

<sup>a</sup> Bancroft, 1963.

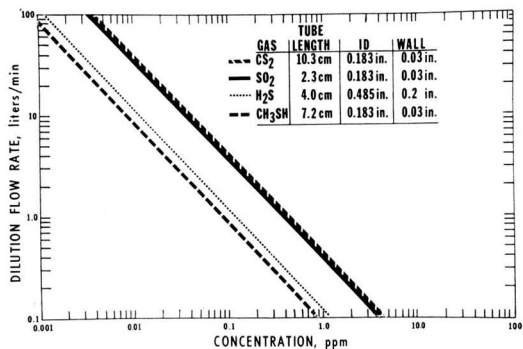


Figure 1. Dilution flow rate vs. sulfur compound concentration

Where:  $C$  = Parts-per-million (V./V.) of permeand transferred to a gas flowing over the tube

$Pr$  = Weight loss (at 20.3° C.) expressed in micrograms per min.

$M$  = Molecular weight

$L$  = Liters per minute

$G$  = Gas Constant = 22.4

**Detector Calibration System.** Figure 2 shows the analytical assembly used for this investigation. The permeation tube was housed in a glass vial and immersed in a constant temperature bath. Dry, clean air, conditioned to the temperature of the bath, flowed over the tube and through a four-way rotary valve at a flow rate always greater than the demand of the detector, the excess being vented to the atmosphere. The valving was arranged so that the sample entering the detector consisted of clean air with or without added permeand. The sample was pulled through the detector system by means of a vacuum pump located downstream of the detector.

Sample flow and hydrogen flow through the detector were measured and controlled by metering the gases through precision needle valves and calibrated flowmeters. Gases flowed from the detector into heated tubing to prevent condensation of water in the vacuum pump. Additional air was pulled into the exit gas line to further assist in preventing condensation.

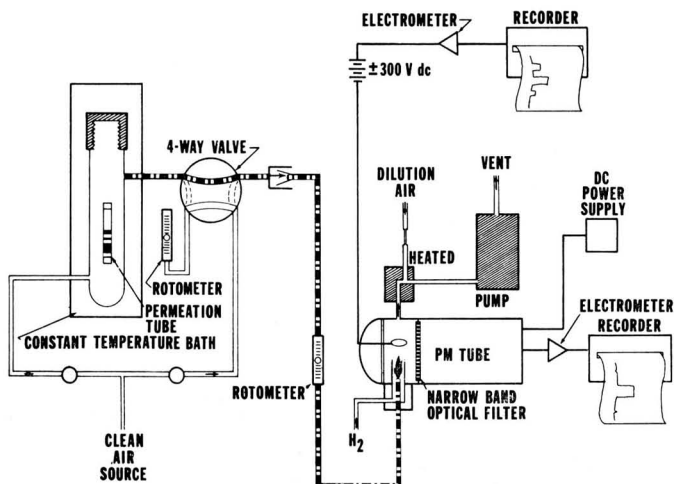


Figure 2. Diagram of calibration system

Figure 3 shows detector response as a function of sample carrier gas flow for methyl mercaptan. From the graph we note that flow changes of 5% changed the response about 4%. This response change was typical for all the gases studied. Hydrogen flow changes between 200 and 240 ml. per minute had virtually no effect on detector response.

### Results and Discussion

**Detector Response.** The response characteristics of the FPD for sulfur dioxide, hydrogen sulfide, methyl mercaptan, and carbon disulfide are represented graphically in Figure 4. Methyl mercaptan produced a slightly higher response than was expected in comparison with the other mono-sulfur species studied. This response may be due to losses in the tubing, attributable to greater reactivity of SO<sub>2</sub> and H<sub>2</sub>S.

Detector response deviates from a straight line relation (log-log scale) above one part-per-million (V./V. basis) for sulfur compounds whose sulfur contents exceed 50% by weight.

The response of the detector is directly related to the concentration of sulfur entering the detector per unit time. This important relationship is tabulated (Table II) and shown graphically in Figure 5. The FPD calibrated in this manner can serve as a means of determining the concentration in grams of sulfur per unit volume of ambient air. This system can also serve as a secondary means of calibrating the output of permeation tubes containing SO<sub>2</sub>, in a manner similar to that described by Scaringelli, Frey, *et al.* (1967) in their experiments with a microcoulometric detector.

The calibration of the FPD is quite stable, as evidenced by repeated checks of several points over a 3-month period. Performance of the detector is unaffected by the temperature of its housing, over the range 80 to 120° C.

**Sample Transfer Tubing.** Fluorinated ethylene-propylene copolymer (FEP Teflon) tubing (1/16-inch i.d. and 0.03-inch wall thickness) was used to transfer the sample from the outlet of the permeation tube to the inlet of the detector system. Various samples of 303 stainless steel tubing were tested as sample transfer lines. The results were startling, in that certain lengths of stainless steel tubing prevented the sulfur dioxide from reaching the detector, while other pieces from the same supplier compared favorably with Teflon. Cleaning the tubing with methylene chloride, acetone, and water failed

to improve the stainless tubing's transfer properties. Studies are continuing to determine the conditions under which stainless tubing exhibits poor transfer of  $\text{SO}_2$ .

**Flame Photometric Detector as an Atmospheric Sulfur Dioxide Analyzer—A Preliminary Study.** The flame photometric detector was arranged to draw atmospheric air through a glass microfiber filter (to remove particulates, including sulfuric acid) into 6 feet of Teflon tubing leading to the inlet of the detector. Figure 6 shows a continuous  $\text{SO}_2$  analysis of the ambient air outside the fourth floor of our laboratory

building in Cincinnati, Ohio. The results of these experiments encouraged the initiation of a program to evaluate the FPD as a routine continuous  $\text{SO}_2$  ambient air monitor. Concurrently with these studies, development of a specific  $\text{SO}_2$  scrubber, similar to that described by Adams, Bamesberger, *et al.* (1968), is planned, since the detector responds to all sulfur species. By determining the difference between ambient air-total sulfur and ambient air minus  $\text{SO}_2$ , a real  $\text{SO}_2$  concentration can be realized. In urban areas, almost all of the sulfur in the atmosphere is thought to exist as  $\text{SO}_2$ . If  $\text{SO}_2$  can be

Figure 3. Detector response as a function of air flow rate to detector

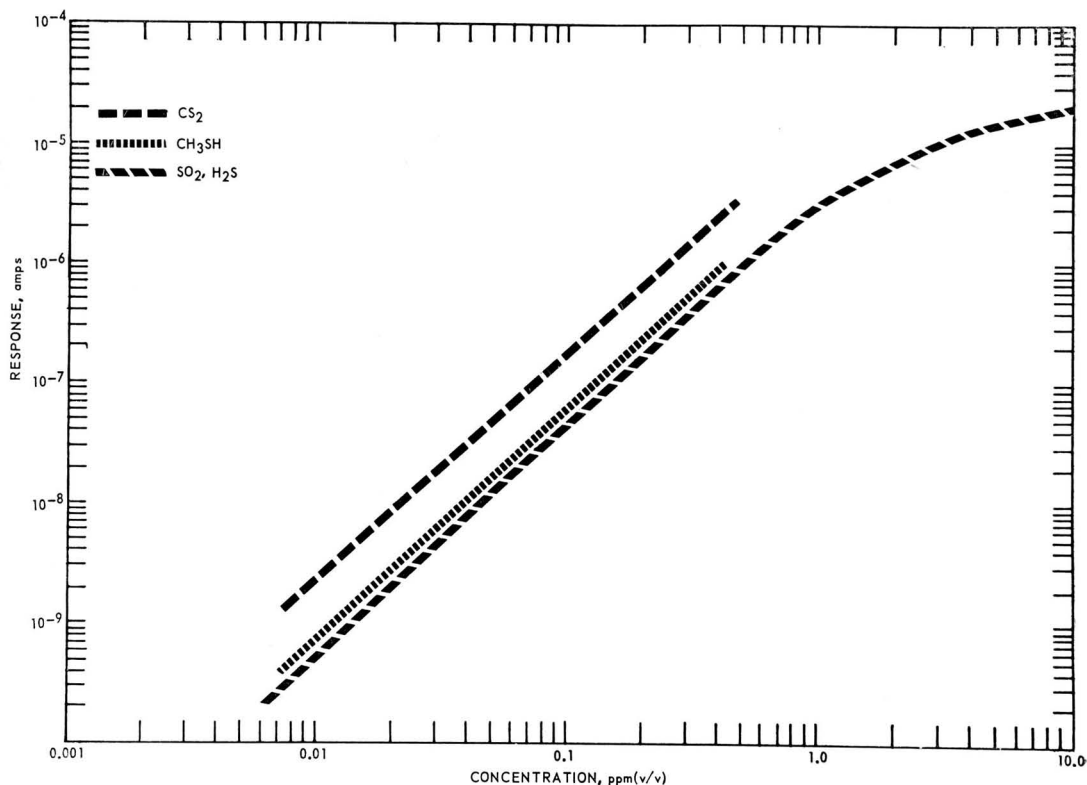
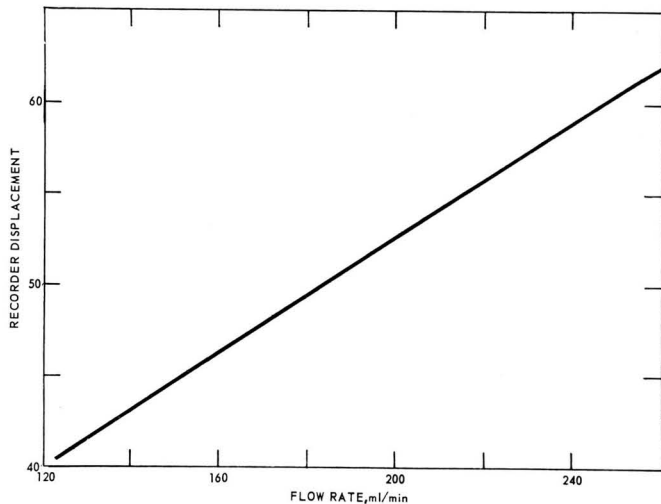


Figure 4. Detector response *vs.* concentration, for several sulfur compounds

Figure 5. Detector responses of several compounds, as functions of their sulfur content

Sample	Response amps ng. <sup>-1</sup> sec. <sup>-1</sup>
SO <sub>2</sub>	5.5 × 10 <sup>-8</sup>
CH <sub>3</sub> SH	9.0 × 10 <sup>-8</sup>
H <sub>2</sub> S	1.75 × 10 <sup>-7</sup>
CS <sub>2</sub>	1.4 × 10 <sup>-7</sup>
Butane	1.0 × 10 <sup>-13</sup>

Values taken at a sample flow of 180 ml. per min. into detector. Background current with flame on = 2 × 10<sup>-9</sup> amps. Electrometer setting at 1% noise level = 3 × 10<sup>-9</sup> amps.

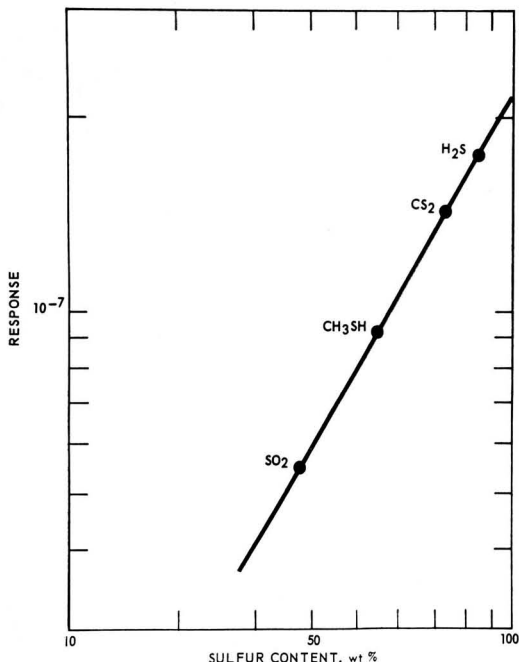


Table II. Response of Flame Photometric Detector to Several Compounds

Sample	Response Expressed in Amp. Sec. Ng. <sup>-1</sup>
SO <sub>2</sub>	5.5 × 10 <sup>-8</sup>
CH <sub>3</sub> SH	9.0 × 10 <sup>-8</sup>
H <sub>2</sub> S	1.75 × 10 <sup>-7</sup>
CS <sub>2</sub>	1.4 × 10 <sup>-7</sup>
Butane	1 × 10 <sup>-13</sup>

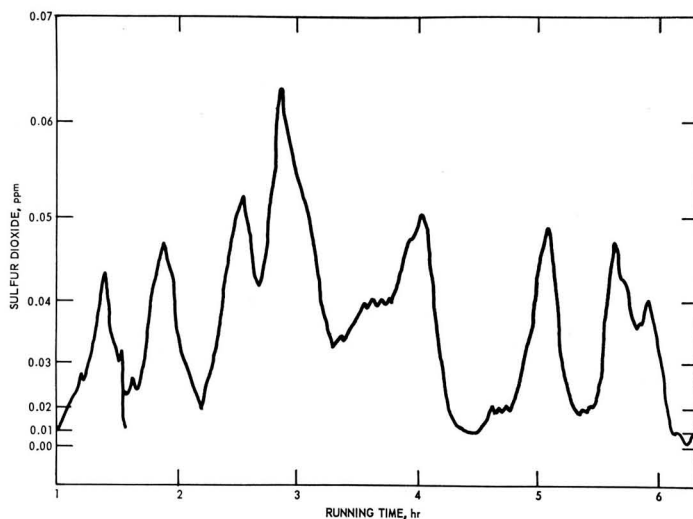


Figure 6. Recording of ambient SO<sub>2</sub> concentration

clearly demonstrated to be the predominant sulfur-bearing gas, the need for a selective scrubber would become less critical.

#### Acknowledgment

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# Solubility of Gypsum in Aqueous Electrolytes as Affected by Ion Association and Ionic Strengths up to 0.15M and at 25° C.

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■ A computer program is utilized to calculate ion association and solubility of gypsum in aqueous electrolyte systems (NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, CaSO<sub>4</sub>, or their mixtures) of limited ionic strength and at 25° C. The Fortran program accepts nonequilibrium input solute concentrations and considers simultaneously the Debye-Hückel theory,  $K_{SP}$  of gypsum, and  $K_D$  of CaSO<sub>4</sub><sup>°</sup>, MgSO<sub>4</sub><sup>°</sup>, and NaSO<sub>4</sub><sup>-</sup> to predict equilibrium concentrations without prior measurement in the equilibrium state. Predicted cationic activities and stoichiometric solubility of gypsum are in general agreement with observed values in this and other studies. This computer approach provides a comprehensive description of various solution parameters heretofore not fully realized for the above systems.

Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) is frequently present in the soil or underlying stratum in arid regions and may be the principal salt causing pronounced salinity in the natural waters of such regions. In agriculture, gypsum is commonly applied as a soil amendment to reclaim sodium-affected soils and as a water amendment to reduce the sodium hazard of irrigation waters. Because substantial salinity may be contributed to soil solutions, and surface and ground water supplies by gypsum (Tanji, Doneen, *et al.*, 1967), quantitative predictions on its solubility would have significance in agriculture, hydrochemistry, and geochemistry.

The earlier studies on the solubility of gypsum in water and other aqueous systems have been reported by Cameron and Bell (1906) and Seidell and Linke (1958). More recently, gypsum solubility at or near 25° C. and in aqueous salt solutions of limited concentrations have been published by Longenecker and Lyerly (1959), Denman (1961), and Nakayama and Rasnick (1967). Among others the solubility of CaSO<sub>4</sub>·2H<sub>2</sub>O, CaSO<sub>4</sub>·½ H<sub>2</sub>O, and CaSO<sub>4</sub> in aqueous systems up to 6 molal concentration and to 200° C. have been reported by Bock (1961), Marshall, Slusher, *et al.* (1964), Power, Fabuss, *et al.* (1966), Marshall and Slusher (1966), Ostroff and Metler (1966), Metler and Ostroff (1967), and Marshall and Slusher (1968). These and other investigators have predicted the solubility of gypsum with varying degrees of precision on the basis of empirical and theoretical considerations.

Many of the current studies on the solubility of calcium sulfates are concerned with scaling problems in desalination and other industrial processes involving elevated temperatures. For low temperature-low electrolyte concentration systems, gypsum solubility needs to be examined more comprehensively, particularly its solubility as affected by ion association. Reported herein is an extension of a previous computer technique (Tanji and Doneen, 1966) to predict various solution parameters in aqueous electrolytes undersaturated or saturated with respect to gypsum. These solution parameters in-

clude dissociated concentrations of Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup>, ion pairs of CaSO<sub>4</sub><sup>°</sup>, MgSO<sub>4</sub><sup>°</sup>, and NaSO<sub>4</sub><sup>-</sup>, ionic strength corrected for ion association, ionic activities, and stoichiometric solubility of gypsum in simple and mixed salt solutions up to 0.15M ionic strength and at 25° C.

## Experimental

Aqueous salt solutions were prepared from Baker Analyzed Reagent Grade chemicals. Various salt concentrations were prepared by diluting 0.1M stock solutions with distilled water. These concentrations were then checked by specific conductance with a conductivity bridge meter (Model RC-16B2, Industrial Instruments, Inc.). For aqueous electrolytes prepared from highly deliquescent salt (CaCl<sub>2</sub>·2H<sub>2</sub>O and MgCl<sub>2</sub>·6H<sub>2</sub>O) the solutions were within ±2% of the desired concentrations while other solutions were within ±0.5%. Baker Analyzed Reagent Grade CaSO<sub>4</sub>·2H<sub>2</sub>O (powder) was also used.

The solubility studies were carried out in glass flasks for 24 hours, continuously on a wrist action shaker, and at 25° ± 1° C. The saturated solutions of gypsum were filtered through No. 41 Whatman filter paper. Filtrates were analyzed for Ca by either flame photometry (Beckman DU Spectrophotometer with photomultiplier attachment) or by titration with ethylenediaminetetraacetic acid (EDTA). Sulfate was determined gravimetrically as BaSO<sub>4</sub>.

The activity of Ca<sup>2+</sup> and Ca<sup>2+</sup> + Mg<sup>2+</sup> was measured respectively with a Ca-electrode (Orion Model 92-20) and a Divalent Cation-electrode (Orion Model 92-32), a single junction reference electrode (Orion Model 90-01), and a digital pH meter (Orion Model 801). These electrodes were used as suggested by the manufacturer's manual. The activity of Na<sup>+</sup> was measured with a sodium-ion glass electrode (Beckman Model 39278) in conjunction with a fiber junction calomel electrode (Beckman Model 39170) and an expandomatic pH meter (Beckman Model 76004).

## Computational Scheme

A Fortran IV computer program has been developed to predict ion association and solubility of gypsum in simple and mixed aqueous electrolyte systems.  $K_{SP}$  of gypsum and  $K_D$  of CaSO<sub>4</sub><sup>°</sup>, MgSO<sub>4</sub><sup>°</sup> and NaSO<sub>4</sub><sup>-</sup> are considered simultaneously. Provisional values on ionic strength, single ion activity coefficients, ionic activities, and other solution parameters are calculated for every predicted chemical change in the system and until equilibrium is attained. By this computer approach, calculations on various parameters can be made from only initial input data without any prior measurement of the equilibrium state. These input data are nonequilibrium stoichiometric concentrations except in systems containing only nonassociated electrolytes. The computer program is capable of predicting ion association in incompletely dissociated electrolytes (Case I), dissolution of excess solid phase gypsum in the presence of electrolytes (Case II), and precipitation of gypsum from admixtures of dissolved salts initially free of solid phase gypsum (Case III). The source list

for the general case computer program, with detailed description, is available upon request (Tanji, 1968).

The solubility of gypsum is partly described by

$$K_{SP} = \frac{a_{Ca} a_{SO_4} a^2 H_2O}{a_{CaSO_4} \cdot 2H_2O} = m_{Ca} \gamma_{Ca} m_{SO_4} \gamma_{SO_4} \quad (1)$$

with  $K_{SP}$  equal to  $2.4 \times 10^{-5}$  (Latimer, 1952). This and following constants are for 25° C. unless specified. Other  $K_{SP}$  values in the literature range from  $2.45 \times 10^{-5}$  (Moreno and Osborn, 1963),  $2.50 \times 10^{-5}$  (Nakayama and Rasnick, 1967) to  $4.23 \times 10^{-5}$  (Marshall and Slusher, 1966),  $4.236 \times 10^{-5}$  (Marshall and Slusher, 1968), and  $4.52 \times 10^{-5}$  at 28° C. (Ostroff and Metler, 1966). The activities of  $CaSO_4 \cdot 2H_2O$  and  $H_2O$  are arbitrarily taken at unity. The activity,  $a_i$ , of the subscripted ion species  $i$  is defined by  $m_i \gamma_i$  representing the molar concentration and ionic activity coefficient, respectively. Although it is recognized that some question exists on the measurement and meaning of single-ion activities (Guggenheim, 1935; Pitzer, Brewer, *et al.*, 1961), estimates on activity coefficients of individual ions do have physical significance (Alfenaar and De Ligny, 1967) and are necessary for computations in mixed electrolyte systems.

Ionic activity coefficients ( $\gamma_i$ ) may be computed from the Debye-Hückel expression

$$\log \gamma_i = -(0.509 z_i^2 \mu^{1/2}) / (1 + B \bar{a} \mu^{1/2}) \quad (2)$$

where  $z$  is the valence of the ion species  $i$ ,  $\mu$  is the ionic strength calculated by  $\frac{1}{2} \sum_{i=1}^n m_i z_i^2$  of all the dissociated solutes present,  $B$  is taken as 0.33, and  $\bar{a}$  is the ion size parameter. Another equation approximating  $\gamma_i$  takes a fixed value of 3A for  $\bar{a}$  so that  $B\bar{a}$  reduces to unity and contains a deviation parameter  $b$

$$\log \gamma_i = -0.509 z_i^2 (\mu^{1/2} / (1 + \mu^{1/2}) - b\mu) \quad (3)$$

that may be taken as 0.2 for many electrolytes (Davies, 1962). Equation 3 without  $\bar{a}$  as the adjustable parameter was used in this work because it has provided predictions on solubility of gypsum (Tanji and Doneen, 1966) which substantially agree with those using Equation 2 for limited  $\mu$ .

For dissolution of gypsum (Case II) let  $m^{\circ}_{Ca}$  and  $m^{\circ}_{SO_4}$  be the initial molar concentrations of undissociated  $Ca^{2+}$  and  $SO_4^{2-}$ , and let  $X$  be the amount that dissolves from gypsum. Then  $m_{Ca} = m^{\circ}_{Ca} + X$  and  $m_{SO_4} = m^{\circ}_{SO_4} + X$ . Combining  $m_{Ca}$  and  $m_{SO_4}$  into Equation 1 yields

$$[\gamma_{Ca} \gamma_{SO_4}] X^2 + [\gamma_{Ca} \gamma_{SO_4} (m^{\circ}_{Ca} + m^{\circ}_{SO_4})] X + [m^{\circ}_{Ca} \gamma_{Ca} m^{\circ}_{SO_4} \gamma_{SO_4} - K_{SP}] = 0 \quad (4)$$

from which  $X$  may be obtained by iteration. For precipitation of gypsum (Case III) let  $W$  be the amount that precipitates so that  $m_{Ca} = m^{\circ}_{Ca} - W$  and  $m_{SO_4} = m^{\circ}_{SO_4} - W$ . An expression similar to Equation 4 is obtained to compute precipitation when  $m_{Ca}$  and  $m_{SO_4}$  are combined with Equation 1.

Increases in the stoichiometric solubility of gypsum occur if  $Ca^{2+}$  and/or  $SO_4^{2-}$  associates into ion pairs ( $CaSO_4^{\circ}$ ,  $MgSO_4^{\circ}$ ) and complexes ( $NaSO_4^-$ ,  $KSO_4^-$ ). The dissociation constant ( $K_D$ ) of ion pair  $CaSO_4^{\circ}$  can be expressed as

$$K_D = \frac{m_{Ca} \gamma_{Ca} m_{SO_4} \gamma_{SO_4}}{m_{CaSO_4^{\circ}} \gamma_{CaSO_4^{\circ}}} \quad (5)$$

in which  $K_D$  is taken as  $4.9 \times 10^{-3}$  from solubility data (Bell and George, 1953) in good agreement with  $5.00 \times 10^{-3}$  from emf (Nancollas, 1957) but in variance with  $1.26 \times 10^{-2}$  (Marshall and Slusher, 1966). The  $\gamma_{CaSO_4^{\circ}}$  is assumed to be unity. If  $m^{\circ}_{Ca}$ ,  $m^{\circ}_{SO_4}$ , and  $m^{\circ}_{CaSO_4}$  are the initial molar concentrations of  $Ca^{2+}$ ,  $SO_4^{2-}$ , and  $CaSO_4^{\circ}$ , respectively, and  $Y$  is the quantity of  $CaSO_4^{\circ}$  formed, then  $m_{Ca} = m^{\circ}_{Ca} - Y$ ,  $m_{SO_4} = m^{\circ}_{SO_4} - Y$ , and  $m_{CaSO_4^{\circ}} = m^{\circ}_{CaSO_4^{\circ}} + Y$ . Combining  $m_{Ca}$ ,  $m_{SO_4}$ , and  $m_{CaSO_4^{\circ}}$  into Equation 5 results in

$$[\gamma_{Ca} \gamma_{SO_4}] Y^2 - [\gamma_{Ca} \gamma_{SO_4} (m^{\circ}_{Ca} + m^{\circ}_{SO_4}) + K_D \gamma_{CaSO_4^{\circ}}] Y + [m^{\circ}_{Ca} \gamma_{Ca} m^{\circ}_{SO_4} \gamma_{SO_4} - K_D m^{\circ}_{CaSO_4^{\circ}} \gamma_{CaSO_4^{\circ}}] = 0 \quad (6)$$

from which the theoretical concentration of the ion pair ( $m^{\circ}_{CaSO_4^{\circ}} + Y$ ) may be calculated.

At this stage of computation, the stoichiometric solute concentrations of Ca and  $SO_4$  are  $m_{Total Ca} = m_{Ca} + m_{CaSO_4^{\circ}}$  and  $m_{Total SO_4} = m_{SO_4} + m_{CaSO_4^{\circ}}$ . In saturated gypsum solutions at 25° C. the maximum  $CaSO_4^{\circ}$  concentration possible is 4.898 mM./L. ( $m_{CaSO_4^{\circ}} = K_{SP}/K_D \gamma_{CaSO_4^{\circ}}$ ) because the num-

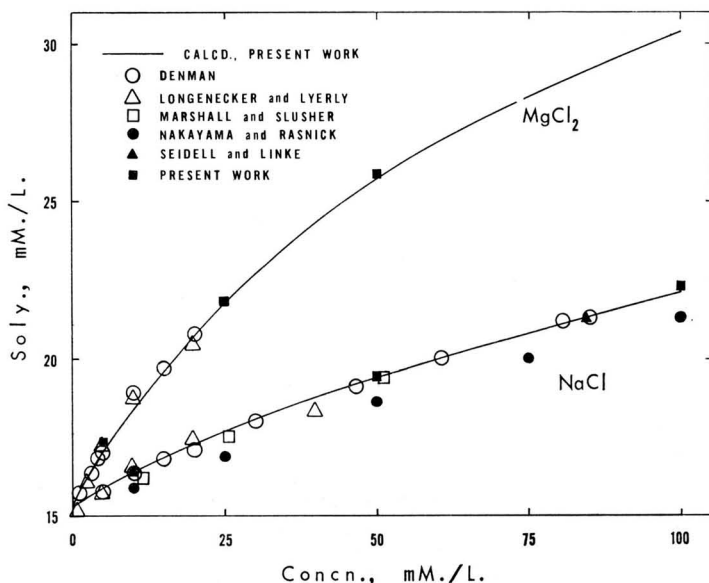


Figure 1. Solubility of gypsum in various concentrations of NaCl and  $MgCl_2$  solutions at or near 25° C.

erator of Equation 5 is identical to  $K_{SP}$ , Equation 1, which is a fixed value at a given temperature.

The dissociation constant for  $MgSO_4^\circ$  is defined by

$$K_D = \frac{m_{Mg} \gamma_{Mg} m_{SO_4} \gamma_{SO_4}}{m_{MgSO_4} \gamma_{MgSO_4}} \quad (7)$$

in which  $\gamma_{MgSO_4}^\circ$  is taken at unity and  $K_D$  as  $6.3 \times 10^{-3}$  (Money and Davies, 1932). By substituting  $m^\circ_{Mg}$  and  $m^\circ_{MgSO_4}$ , respectively, for  $m^\circ_{Ca}$  and  $m^\circ_{CaSO_4}$ , an expression similar to Equation 6 can be obtained to compute  $MgSO_4^\circ$ .

The above  $K_D$  of  $MgSO_4^\circ$  based on conductance method is in agreement with  $6.06 \times 10^{-3}$  obtained from ultrasonics by Atkinson and Petrucci (1966).  $K_D$  has also been reported to be  $4.27 \times 10^{-3}$  (Nancollas, 1957) and  $4.36 \times 10^{-3}$  (Jones and Monk, 1952) on the basis of emf method. Recently Marshall (1967) obtained a  $K_D$  of  $3.99 \times 10^{-3}$  from solubility data. A computer run using Marshall's  $K_{SP}$  of  $4.24 \times 10^{-5}$ ,  $K_D$  of  $1.26 \times 10^{-2}$  for  $CaSO_4^\circ$  and  $3.99 \times 10^{-3}$  for  $MgSO_4^\circ$  yielded gypsum solubility values that were much higher than those in the literature and those predicted by using the constants indicated in this paper. An examination of Figure 2 in Marshall's (1967) paper shows that most of the literature values for  $MgSO_4^\circ$  at or near 25° C. are higher than  $3.99 \times 10^{-3}$  but this does not preclude that his  $K_D$  and other constants are more acceptable for computational procedures, equations, and parameters used elsewhere (Marshall and Slusher, 1968).

For  $NaSO_4^-$  the  $K_D$  is described by

$$K_D = \frac{m_{Na} \gamma_{Na} m_{SO_4} \gamma_{SO_4}}{m_{NaSO_4} - \gamma_{NaSO_4^-}} \quad (8)$$

having a value of  $1.9 \times 10^{-1}$  (Jenkins and Monk, 1950). Following the same technique for computing neutral ion pairs, the theoretical  $NaSO_4^-$  concentration may be calculated.  $NaSO_4^-$  is taken as a charged complex for which  $\gamma_{NaSO_4^-}$  is calculated and  $m_{NaSO_4^-}$  is included in  $\mu$  while  $CaSO_4^\circ$  and  $MgSO_4^\circ$  are not. The stoichiometric concentrations of various solute species are then:  $m_{Total\ Ca} = m_{Ca} + m_{CaSO_4^\circ}$ ,  $m_{Total\ SO_4} = m_{SO_4^\circ} + m_{MgSO_4^\circ} + m_{NaSO_4^-} + m_{CaSO_4^\circ}$ ,  $m_{Total\ Mg} = m_{Mg} + m_{MgSO_4^\circ}$ , and  $m_{Total\ Na} = m_{Na} + m_{NaSO_4^-}$ . Unlike  $CaSO_4^\circ$  the concentrations of  $MgSO_4^\circ$  and  $NaSO_4^-$  are not usually limited because their ion activity products

may increase to large values without exceeding the  $K_{SP}$  of their respective salts, except in concentrated brines.

### Ion Activity and Association

The aforementioned computing procedure was applied to several aqueous electrolytes (Case I). Table I contains some of the calculated parameters for various concentrations of these salt solutions. Significant amounts of ion pairs were computed, even at these limited salt concentrations, for the incompletely dissociated sulfate solutions. Also tabulated are  $\mu$ , corrected for ion pairs in associated electrolytes, and mono- and divalent ion activity coefficients ( $\gamma_1$  and  $\gamma_2$ , respectively). As a check on the computed single ion activity coefficients, mean activity coefficients ( $\gamma_{\pm}$ ) of the dissolved salts were calculated independently from  $(\gamma_+^{\nu+} \gamma_-^{\nu-})^{1/\nu}$  using the computed  $\gamma_1$  and  $\gamma_2$  values. The  $\gamma_{\pm}$  (Pitzer, Brewer, *et al.*, 1961) so calculated were in close agreement with literature  $\gamma_{\pm}$  values for all concentrations of NaCl but not so close for other electrolytes, particularly  $MgSO_4$ . These deviations mainly are due to the use of Equation 3 in which  $\bar{a}$  is taken as 3A for all ions and  $b$  as 0.2 for all electrolytes. Also, the variations of calculated  $\gamma_{\pm}$  from measured  $\gamma_{\pm}$  in unsymmetrical electrolytes are partly the result of taking a geometric mean of the potential errors in estimating  $\gamma_i$  from Equation 3. For example, if the calculated  $\gamma_2$  for 0.05M  $CaCl_2$  was 5% greater, the resultant calculated  $\gamma_{\pm}$  would be 16% greater than the initial 0.558. Calculated ionic activities of  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Na^+$  from computer analyses agreed with measured values, but with larger deviations at higher  $\mu$ . The computational technique employed in this work appears to be applicable to  $\mu$  up to about 0.15M.

### Dissolution of Gypsum

Table II reports the solubility of gypsum in several aqueous electrolytes and in water (Case II) as stoichiometric values, the sum of dissociated and undissociated concentrations. In the presence of uncommon dissolved salts ( $NaCl$  and  $MgCl_2$ ) the solubility of gypsum is described by the analytically determined concentrations of either  $Ca$  or  $SO_4$ . For systems containing a common ion contributed by the electrolyte, gypsum solubility is determined by the stoichiometric concentration

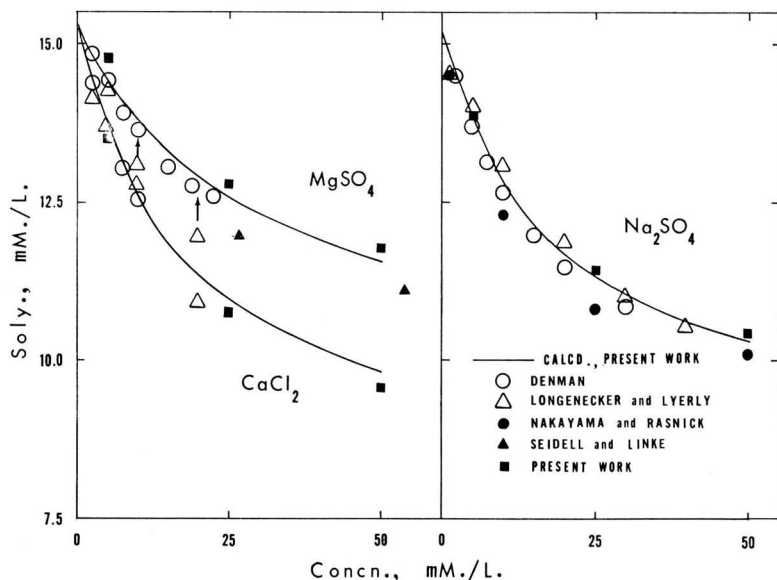


Figure 2. Solubility of gypsum in various concentrations of  $CaCl_2$ ,  $Na_2SO_4$ , and  $MgSO_4$  solutions at or near 25° C.

**Table I. Solution Parameters in Simple Salt Solutions**

Salt Solutions	Calcd. Ion Pair	Calcd. $\mu$	Calcd. $\gamma_{\pm}^a$	Calcd. $\gamma_2^a$	Calcd. $\gamma_{\pm}^b$	Measured $\gamma_{\pm}$	Calcd. Cationic Activity	Measured Cationic Activity
	mM./L.	mM./L.	L./M.	L./M.	L./M.	L./M.	mM./L.	mM./L.
0.010M NaCl	—	10.0	0.901	—	0.901	0.902 <sup>c</sup>	9.01	7.9
0.050M NaCl	—	50.0	0.817	—	0.817	0.818 <sup>c</sup>	40.8	40.0
0.100M NaCl	—	100.0	0.772	—	0.772	0.778 <sup>c</sup>	77.2	77.0
0.005M CaCl <sub>2</sub>	—	15.0	0.883	0.608	0.780	0.784 <sup>c</sup>	3.04	3.1
0.025M CaCl <sub>2</sub>	—	75.0	0.791	0.392	0.626	0.64 <sup>c</sup>	9.79	10.0
0.050M CaCl <sub>2</sub>	—	150.0	0.747	0.311	0.558	0.583 <sup>c</sup>	15.6	17.0
0.005M MgCl <sub>2</sub>	—	15.0	0.883	0.608	0.780	0.792 <sup>c</sup>	3.04	3.2
0.025M MgCl <sub>2</sub>	—	75.0	0.791	0.392	0.626	0.65 <sup>c</sup>	9.79	11.0
0.050M MgCl <sub>2</sub>	—	150.0	0.747	0.311	0.558	0.59 <sup>c</sup>	15.6	18.0
0.005M Na <sub>2</sub> SO <sub>4</sub>	0.15 <sup>d</sup>	14.7	0.884	0.611	0.781	0.778 <sup>c</sup>	8.70	8.6
0.025M Na <sub>2</sub> SO <sub>4</sub>	2.28 <sup>d</sup>	70.4	0.795	0.400	0.632	0.62 <sup>e</sup>	37.9	36.0
0.050M Na <sub>2</sub> SO <sub>4</sub>	6.80 <sup>d</sup>	136.4	0.753	0.321	0.567	0.529 <sup>e</sup>	70.2	69.0
0.005M MgSO <sub>4</sub>	0.94 <sup>f</sup>	16.3	—	0.598	0.598	0.48 <sup>e</sup>	2.43	2.3
0.025M MgSO <sub>4</sub>	7.68 <sup>f</sup>	69.3	—	0.402	0.402	0.30 <sup>e</sup>	6.96	6.8
0.050M MgSO <sub>4</sub>	17.69 <sup>f</sup>	129.2	—	0.327	0.327	0.22 <sup>e</sup>	10.6	12.0
0.005M CaSO <sub>4</sub>	1.12 <sup>h</sup>	15.5	—	0.604	0.604	—	2.34	2.2
0.010M CaSO <sub>4</sub>	2.84 <sup>h</sup>	28.6	—	0.521	0.521	—	3.73	3.8
0.0125M CaSO <sub>4</sub>	3.78 <sup>h</sup>	34.9	—	0.494	0.494	—	4.31	4.3
0.0153M CaSO <sub>4</sub>	4.90 <sup>h</sup>	41.8	—	0.469	0.469	—	4.90	4.8

<sup>a</sup> Mono- and divalent activity coefficients, <sup>b</sup> from  $(\gamma_+^V + \gamma_-^V)^{1/V}$ , <sup>c</sup> from Harned and Owen (1958), <sup>d</sup> NaSO<sub>4</sub><sup>-</sup>, <sup>e</sup> from Glasstone (1947), <sup>f</sup> MgSO<sub>4</sub><sup>o</sup>, <sup>g</sup> from Fedoroff (1941), <sup>h</sup> CaSO<sub>4</sub><sup>o</sup>.

**Table II. Solubility of Gypsum in Single Salt Solutions, 25° C.**

Excess Gypsum + Salt Solutions	Computed Parameters					Measured $a_{Ca}$ mM./L.	Calcd. Soly.	Measured Soly.	
	Ca <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup> mM./L.	Ion pairs <sup>a</sup>	$\gamma_2$ L./M.	$a_{SO_4}$				
Distilled Water	10.44	10.44	4.90 <sup>a</sup>	0.469	4.90	4.90	4.8	15.34	15.30
0.010M NaCl	11.45	11.28	0.18 <sup>b</sup>	0.431	4.86	4.94	4.8	16.35	16.47
0.050M NaCl	14.52	13.57	0.95 <sup>b</sup>	0.349	4.74	5.07	5.0	19.42	19.42
0.100M NaCl	17.24	15.34	1.90 <sup>b</sup>	0.301	4.62	5.19	5.3	22.14	22.30
0.005M MgCl <sub>2</sub>	12.12	11.14	0.98 <sup>c</sup>	0.422	4.70	5.11	5.4	17.02	17.37
0.025M MgCl <sub>2</sub>	16.85	13.26	3.59 <sup>c</sup>	0.328	4.35	5.52	5.8	21.75	21.82
0.050M MgCl <sub>2</sub>	20.68	14.88	5.80 <sup>c</sup>	0.279	4.16	5.78	6.4	25.58	25.86
0.005M CaCl <sub>2</sub>	13.80	8.80	4.90 <sup>a</sup>	0.444	3.91	6.13	6.0	13.70	13.50
0.025M CaCl <sub>2</sub>	31.06	6.06	4.90 <sup>a</sup>	0.357	2.16	11.09	11.0	10.96	10.75
0.050M CaCl <sub>2</sub>	54.90	4.90	4.90 <sup>a</sup>	0.299	1.46	16.40	15.0	9.80	9.56
0.005M Na <sub>2</sub> SO <sub>4</sub>	8.91	13.61	0.30 <sup>b</sup>	0.445	6.06	3.96	3.8	13.81	13.84
0.025M Na <sub>2</sub> SO <sub>4</sub>	6.41	28.52	2.88 <sup>b</sup>	0.362	10.34	2.32	2.6	11.30	11.41
0.050M Na <sub>2</sub> SO <sub>4</sub>	5.36	47.40	7.97 <sup>b</sup>	0.307	14.56	1.65	1.8	10.26	10.41
0.005M MgSO <sub>4</sub>	9.52	13.12	1.40 <sup>c</sup>	0.438	5.75	4.17	5.0	14.41	14.84
0.025M MgSO <sub>4</sub>	7.68	23.97	8.71 <sup>c</sup>	0.361	8.65	2.77	2.9	12.58	12.78
0.050M MgSO <sub>4</sub>	6.63	37.35	19.28 <sup>c</sup>	0.311	11.63	2.06	2.1	11.53	11.76

<sup>a</sup> 4.90 mM./L. CaSO<sub>4</sub><sup>o</sup> in all solutions, <sup>b</sup> NaSO<sub>4</sub><sup>-</sup>, <sup>c</sup> MgSO<sub>4</sub><sup>o</sup>.

of SO<sub>4</sub> in the Ca-electrolyte and by stoichiometric Ca in SO<sub>4</sub>-electrolytes.

The measured solubility of gypsum in distilled water was 15.30 which compares favorably with literature values ranging from 15.0 to 15.4 mmoles per liter (Seidell and Linke, 1958). The computed solubility of 15.34 mmoles per liter consists of 10.44 mmoles per liter of uncomplexed Ca<sup>2+</sup> or SO<sub>4</sub><sup>2-</sup> and 4.90 mmoles per liter of undissociated CaSO<sub>4</sub><sup>o</sup>.

The computed ionic activities of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> are 4.90 mmoles per liter.

In the presence of increasing concentrations of NaCl, the solubility of gypsum is increasingly enhanced because of decreases in activity coefficient and increases in NaSO<sub>4</sub><sup>-</sup> complexation. Owing to the association of SO<sub>4</sub><sup>2-</sup> with Na<sup>+</sup>, the activity of SO<sub>4</sub><sup>2-</sup> decreases and concurrently the activity of Ca<sup>2+</sup> increases, as governed by the  $K_{SP}$ . Gypsum solubility



in  $\text{MgCl}_2$  is greater than in  $\text{NaCl}$  owing to a higher  $\mu$  and greater association of  $\text{MgSO}_4^\circ$ , as compared to  $\text{NaSO}_4^-$ , which further reduces the activity of  $\text{SO}_4^{2-}$ . It is commonly held that  $\text{NaCl}$  and  $\text{MgCl}_2$  are uncommon salts relative to gypsum but these data show that they are not uncommon salts in the strictest sense for the cations associate with  $\text{SO}_4^{2-}$  and only in distilled water are the activities of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  identical.

In the presence of a common ion,  $\text{Ca}^{2+}$  from  $\text{CaCl}_2$  or  $\text{SO}_4^{2-}$  from  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$ , the solubility of gypsum is repressed as a result of an increase in activity of the common ion and decrease in activity of the other ion,  $\text{SO}_4^{2-}$  or  $\text{Ca}^{2+}$ , respectively. With increasing electrolyte concentration, the solubility is further reduced. The dissolution of gypsum in  $\text{Na}_2\text{SO}_4$  is greater than in  $\text{CaCl}_2$  because of  $\text{NaSO}_4^-$  complexation and less than in  $\text{MgSO}_4$  because  $\text{MgSO}_4^\circ$  association is stronger than  $\text{NaSO}_4^-$ . Because of the incorporation of  $\text{NaSO}_4^-$  and more refined procedures for computing  $\text{MgSO}_4^\circ$ , the calculated solution parameters in the present work differ slightly from predictions made by an earlier program (Tanji and Doneen, 1966).

The computed and measured stoichiometric solubility of gypsum in various electrolytes are compared with other literature solubility values in Figures 1 and 2. Agreement between predicted and observed solubilities were generally good with greater variations in  $\text{MgSO}_4$  systems.

Calculated  $\text{Ca}^{2+}$  activities (Table II) in different gypsum saturated solutions fitted measured activities. Recently Nakayama and Rasnick (1967) have reported  $\text{Ca}^{2+}$  activities for similar systems which are slightly different from this work, namely, 5.4 mmoles per liter in distilled water; 5.3, 5.6, and 5.9 mmoles per liter, respectively, in 0.01, 0.05, and 0.10M  $\text{NaCl}$ ; and 2.6 and 2.0 mmoles per liter, respectively, in 0.025 and 0.05M  $\text{Na}_2\text{SO}_4$ . Figure 1 shows that Nakayama and Rasnick's solubility data in  $\text{NaCl}$  are lower than other literature values while in  $\text{Na}_2\text{SO}_4$  their data fit closer. Currently there is a great deal of interest on measurement of ion activities with specific ion electrodes (Eisenman, 1968, Shatkey, 1967a). Previous studies (Bower, 1959; Uehara and Mortland, 1960; Thompson, 1966; Thompson and Ross, 1966; Nakayama and Rasnick, 1967) have indicated practical applications of such electrodes. The presence of and effect of foreign or interfering ions are currently being investigated (Ross, 1967; Shatkey, 1967b).

To further illustrate the utility of this computer program, predictions on gypsum solubility in mixed aqueous systems are given in Table III. The calculated solubilities are shown to be in close agreement with measured values for  $\mu$  up to about 0.2M and less accurate for higher  $\mu$ .

#### Precipitation of Gypsum

Another application of the general case computer program is prediction of precipitation in admixtures of salt solutions initially free of solid phase gypsum (Case III). In Mixture 1 of Table IV the calculated dissociated  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations are considerably less than the respective 25 and 12.5 mmoles per liter analytical (stoichiometric) values since 4.44 of  $\text{CaSO}_4^\circ$  and 0.36 mmoles per liter of  $\text{NaSO}_4^-$  are associated. Gypsum was not formed in this mixture for the ion activity product of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  was less than  $K_{\text{SP}}$ . With a two-fold increase in  $\text{Na}_2\text{SO}_4$ , now Mixture 2, ion association is enhanced and solid phase gypsum was precipitated out. The measured precipitation, obtained by taking the difference between initial and final analytical Ca ( $\text{Ca}^{2+} + \text{CaSO}_4^\circ$ ), was 6.0 mmoles per liter as compared to 6.07 mmoles per liter computed.

Table III. Predictions on Solubility of Gypsum in Mixed Aqueous Salt Solutions

NaCl	MgCl <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub>	Calcd. $\mu$	Calcd. Soly.	Measured Soly.
mM./L.						
9.9	—	2.5	—	58.9	15.5	15.4 <sup>a</sup>
99.0	—	2.5	—	166.8	21.1	21.3 <sup>a</sup>
15.0	—	7.5	—	74.0	14.5	14.2 <sup>a</sup>
30.16	—	7.5	—	92.7	15.6	15.3 <sup>a</sup>
22.56	—	3.75	3.78	85.1	15.5	15.2 <sup>a</sup>
10.0	—	5.0	5.15	74.5	14.1	13.8 <sup>a</sup>
50.1	5.0	—	—	122.3	20.5	21.5 <sup>b</sup>
100.0	5.0	—	—	180.5	23.0	23.9 <sup>b</sup>
266.0	5.15	—	—	361.8	28.1	30.9 <sup>b</sup>
50.1	25.05	—	—	186.5	24.1	28.4 <sup>b</sup>
100.0	25.15	—	—	242.7	25.9	29.8 <sup>b</sup>
50.1	50.0	—	—	264.9	27.2	33.7 <sup>b</sup>

<sup>a</sup> Denman (1961), at 25° C., <sup>b</sup> Ostroff and Metler (1966) at 28° C.

Table IV. Solution Parameters in Mixed Electrolytes and Precipitation of Gypsum

Computed Parameters	CaCl <sub>2</sub> -Na <sub>2</sub> SO <sub>4</sub>		CaCl <sub>2</sub> -MgSO <sub>4</sub>	
	1	Mixture <sup>a</sup> 2	3	4
Ca <sup>2+</sup> , mM./L.	20.56	14.04	20.78	15.25
Mg <sup>2+</sup> , mM./L.	—	—	11.02	20.86
Na <sup>+</sup> , mM./L.	24.64	48.84	—	—
SO <sub>4</sub> <sup>2-</sup> , mM./L.	7.69	12.87	6.79	11.11
CaSO <sub>4</sub> <sup>°</sup> , mM./L.	4.44	4.90	4.22	4.90
MgSO <sub>4</sub> <sup>°</sup> , mM./L.	—	—	1.48	4.14
NaSO <sub>4</sub> <sup>-</sup> , mM./L.	0.36	1.16	—	—
<i>a</i> <sub>Ca<sup>2+</sup></sub> , mM./L.	7.47	4.94	7.35	5.12
<i>a</i> <sub>Ca<sup>2+</sup></sub> , mM./L., measured	7.4	4.8	6.4	6.1
<i>a</i> <sub>SO<sub>4</sub><sup>2-</sup></sub> , mM./L.	2.80	4.52	2.40	3.73
<i>a</i> <sub>Mg<sup>2+</sup></sub> , mM./L.	—	—	3.90	7.00
<i>a</i> <sub>Mg<sup>2+</sup></sub> , mM./L., measured	—	—	3.8	6.3
<i>a</i> <sub>Na<sup>+</sup></sub> , mM./L.	19.13	37.61	—	—
<i>a</i> <sub>Na<sup>+</sup></sub> , mM./L., measured	21.	41.	—	—
Solid Phase Gypsum, mM./L.	0.0	6.07	0.0	4.85
Solid Phase Gypsum, mM./L., measured	0.0	6.0	0.0	4.9

<sup>a</sup> 1 = 0.025M CaCl<sub>2</sub> + 0.0125M Na<sub>2</sub>SO<sub>4</sub>  
 2 = 0.025M CaCl<sub>2</sub> + 0.025M Na<sub>2</sub>SO<sub>4</sub>  
 3 = 0.025M CaCl<sub>2</sub> + 0.0125M MgSO<sub>4</sub>  
 4 = 0.025M CaCl<sub>2</sub> + 0.025M MgSO<sub>4</sub>.

For the  $\text{MgSO}_4$ - $\text{CaCl}_2$  mixtures, the  $\text{Ca}^{2+}$  are slightly higher and  $\text{CaSO}_4^\circ$  and  $\text{SO}_4^{2-}$  lower in Mg than in Na-admixtures due to a stronger association of  $\text{MgSO}_4^\circ$  than  $\text{NaSO}_4^-$ . With  $\text{MgSO}_4$  increased two-fold, Mixture 4, gypsum precipitation of 4.85 mmoles per liter was predicted in close agreement with measured 4.9 mmoles per liter. The measured ionic activities of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were lower than computed values while the reverse was true for  $\text{Na}^+$  activities.

Within limits ( $\mu$  up to 0.15M and at 25° C.) the Fortran computer program has provided comprehensive predictions on solution parameters in aqueous solutions undersaturated or saturated with respect to gypsum. For more concentrated electrolyte systems the solubility of gypsum is underestimated because Equation 3 gives  $\gamma_i$  values that are too small. Further

extensions of the Debye-Hückel equation, such as those employed by Marshall and Slusher (1966), may be in order. For elevated temperatures the 25° C. constants in the program will need to be substituted and  $K_{SP}$  of other forms of  $\text{CaSO}_4$  (Marshall, Slusher, *et al.*, 1964; Glater, Ssutu, *et al.*, 1967) will be required.

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## Removal of Orthophosphates from Aqueous Solutions with Activated Alumina

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■ Removals in excess of 99.9% orthophosphates from aqueous solutions have been effected with activated alumina using fixed beds ranging from 1.97 cm. to 26.0 cm. in height. The concentration in the feed varied from  $c_0 = 10$  mg.  $\text{PO}_4^{3-}$  per liter to  $c_0 = 120$  mg.  $\text{PO}_4^{3-}$  per liter. The removal of orthophosphates from solution is initially accompanied by an exchange with the nitrates present on the solid alumina. This is followed by consecutive reformations of the phosphate deposited on the solid surface with phosphate in solution to effect its further removal. Relationships for the equilibrium and the breakthrough curves are presented.

One of the current problems associated with water pollution involves the control of the level of undesirable nutrients which are responsible for the excess growth of

algae or biological slimes in estuaries. Unless means are provided to collect these contaminants, accelerated eutrophication of the receiving waters will occur. Effective limitation of nitrogen as one of the essential nutrients seems doubtful in view of its availability from the atmosphere and from nitrates leached from the soil. Therefore, considerable effort is presently being exerted in the control of phosphates. Current studies (Dryden and Stern, 1968) show that algal growth rates are inhibited at phosphate concentrations of less than 0.5 mg. per liter and are nearly terminated at concentrations of less than 0.05 mg. per liter while a phosphate concentration of 1 mg. per liter will permit a lush growth. Municipal wastes, unless subjected to a phosphate removal treatment, will usually contain approximately 25 mg. of phosphate per liter and constitute a major source of biological nutrients (Valentine, 1967).

Some of the biological treatment processes for reduction of phosphate concentration in waste water involve the use of activated sludge or a pretreatment concerned with algal growth in a controlled environment. These methods do not fulfill the rigid requirements for tertiary treatment (Weinberger, 1968). More effective for phosphate removal are

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chemical treatments, which are still subject to the costs and problems of sludge handling, its disposal, and neutralization of the effluent.

#### Activated Alumina for Removal of Phosphates

Inorganic phosphates exist in several forms. The most common forms are the orthophosphates ( $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ), pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ), triphosphate ( $\text{P}_3\text{O}_{10}^{5-}$ ), and hexametaphosphate [ $(\text{PO}_3)_6^{3-}$ ]. All these phosphates eventually hydrolyze in an aqueous solution and revert to the ortho form. The resulting three orthophosphate species exist in equilibrium with each other and depend on the pH of the solution.

In 1954, Sinha and Choudhury pointed out that fluoride, phosphate, and arsenate ions can be removed from solutions by contacting with acid treated activated alumina. They observed that phosphate removal was not complete after five days of contacting in a batch system, and that the spent solid could be regenerated with nitrates with no loss of alumina into solution. Furthermore, the removal of phosphate could not be effected if the pH of the solution were less than 3.0. In 1958, Kar, using a radioactive tracer technique in a batch system, concluded that the mechanism of phosphate removal with acid treated activated alumina involves a surface reaction followed by slow diffusion into the inner parts of the alumina. Bogoyavlenskii, Belov, *et al.* (1960) independently report that the removal of phosphate by alumina was not complete after 200 hours of continuous contacting in a batch system at 30° C. Furthermore, no significant temperature dependence was apparent for temperatures below 50° C.

While studying the chemistry of phosphates in soils, Cole and Jackson (1950) treated  $\text{AlCl}_3$  with  $\text{KH}_2\text{PO}_4$  in solution having a pH of 3.8. Using x-ray diffraction techniques on the precipitate formed, they identified it as  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  which corresponds to the naturally occurring mineral "variscite." This observation indicates that despite the fact that at this pH, the phosphate ion in equilibrium is predominantly  $\text{H}_2\text{PO}_4^-$ , the ultimate reaction product involved the anion  $\text{PO}_4^{3-}$ . This result can be accounted for only if there is a release of hydrogen ions into the solution.

In a search for an effective means of removing several forms of phosphates contained in low level radioactive wastes, Yee (1966) has reported the results of columnar studies using acid activated alumina and solutions containing the different forms of soluble phosphates. The results of breakthrough curves indicated that alumina has the lowest capacity for orthophosphates. Yee concluded that Alcoa Alumina Type F1 represents an optimum for effectiveness, economy, and ease of regeneration. Projecting his results to a large scale treatment of municipal wastes, Yee arrives at a cost of \$64 per 1,000,000 gallons, somewhat higher than the cost of presently available methods. In reaching this figure, Yee has included a predominant cost associated with an estimated 8% loss of alumina with each regenerative cycle. This loss, due to the dissolving of alumina in the caustic regenerants, has been conservatively assumed by Yee (1966) to apply to all successive regenerative cycles; however, verification of these assumptions regarding alumina loss must be made before this process can be applied commercially.

#### Experimental

For the phosphate removal studies of this investigation, two borosilicate glass cylindrical reactors were used. One reactor was constructed to accommodate small bed volumes of alumina ( $d = 4.5$  cm., and  $h = 1.97$  cm.) and can be considered a short bed reactor, while the other reactor was built

to handle beds of a longer length ( $d = 4.2$  cm., and  $h = 26$  cm.). A schematic diagram is presented in Figure 1.

The effluent stream from the short bed reactor was continuously removed and samples were periodically withdrawn from the sampling port located just above the fixed bed. In addition to the overflow sample of the long bed reactor, a number of intermediate samples were withdrawn from taps situated at convenient locations along the length of the column. Of necessity, these samples were withdrawn very slowly to establish basic concentration profiles along the length of the reactor. Two 20-liter calibrated borosilicate glass bottles connected to a common outlet, constituted the reservoir for the feed solution. The feed solution was prepared by the addition and mixing of an aliquot sample of a standard concentrated orthophosphate solution to distilled water contained in each of the bottles. A "Vibrostatic" pump (Chemical Rubber Co.), coupled to a voltage reducer, maintained constant flow rates over extended periods of time. To measure the solution flow rates, appropriate rotameters were installed between the pump and the fixed bed reactor.

The alumina, furnished by the Aluminum Company of America, Type F1 was 28- X 48-mesh and was claimed to have a specific surface area of 210 sq. meters per gram, external volume void fraction of about 25%, an internal void fraction of about 0.25 cm<sup>3</sup> per gram and a solid specific

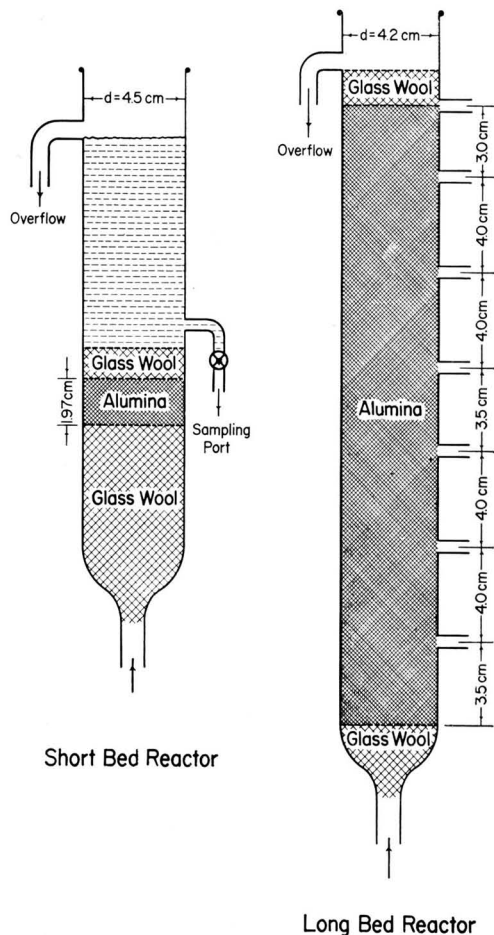
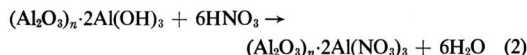
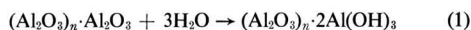


Figure 1. Schematic diagram and basic dimensions of experimental reactors

gravity of 3.3 grams per cm.<sup>3</sup> The bulk packed density was reported to be 55 pounds per cubic foot. The alumina was prepared by first washing it with distilled water, and then contacting it with 1.0*N* nitric acid. There is a strong inference that when alumina is treated in this manner, the following surface reactions occur:



The alumina was then dried overnight in an oven at 125° C. The activation step with nitric acid is a necessary prerequisite to phosphate removal (Yee 1966; Valentine 1967).

The alumina was weighed and its volume was measured in a graduated cylinder after tapping to ensure proper packing. The alumina was then confined between layers of glass wool to ensure plug flow through the interstices of the fixed bed. Glass wool was fitted into each port hole, thus eliminating the passage of alumina into the liquid samples.

A run was initiated when the liquid level was at the top of the fixed bed while the liquid flow rate remained constant. These runs were extensive, and depending on the flow rate and orthophosphate concentration, ranged from 11 to 113 hours in duration. The samples collected were analyzed for phosphate, nitrate, and hydrogen ion concentration.

**Orthophosphate Analysis.** The method outlined by Edwards, Molof, *et al.* (1965) was used to account for orthophosphate concentrations. Ammonium molybdate and potassium antimonyl tartrate are reacted in the presence of sulfuric acid with dilute solutions of orthophosphate to produce the phosphomolybdate ion,  $\text{PO}_4 \cdot 12\text{MoO}_3^{8-}$ . This complex ion is then reduced by the addition of ascorbic acid to produce the intensely colored "molybdenum blue" which reached maximum color intensity within 10 minutes and remained stable for several hours. A calibrated spectrophotometer was then used to establish the orthophosphate concentration of each sample using a wave length of 880  $\mu$ .

**Nitrate Determination.** Colorimetric tests resulting from the interaction of mixed reagents specific for nitrates were used to establish the concentration of this ion. The mixed reagents were supplied by the Hach Chemical Co. (1967) and involved the cadmium reduction method with 1-naphthylamine-sulfanilic acid. The principles and observations outlined by the supplier appear to be similar to those presented by the American Public Health Assoc. (1965). A calibrated spectrophotometer was then used to establish the nitrate concentration of each sample using a wave length of 525  $\mu$ .

**Hydrogen Ion Determination.** A Beckman "Expandomatic pH Meter" was used to establish the hydrogen ion concentration. To make these determinations standard pH buffer solutions were used as references.

**Qualitative Determination for Dissolved Aluminum.** Dissolved aluminum was measured using the reagent "aluminon" (aurintricarboxylic acid) supplied by the Hach Chemical Co. This method is similar to that described at length by the American Public Health Assoc. (1965) and is associated with the generation of a red-to-pink color which exhibits maximum absorption around 525  $\mu$ .

Five runs were conducted using the short bed reactor and two runs using the long bed reactor. For the latter runs, the feed concentration was 120 mg.  $\text{PO}_4^{3-}$  per liter. All runs were carried out at 71° F. For the short bed runs, the feed concentrations were 10 and 30 mg.  $\text{PO}_4^{3-}$  per liter. The operating conditions of these runs for both types of beds are presented in Table I. Since some of these runs extended over a

Table I. Operating Conditions for Short Bed and Long Bed Runs

Run	$c_0$ Mg. $\text{PO}_4^{3-}$ per Liter	F, Feed Rate, Cm. <sup>3</sup> per Minute	Reactor Bed		
			Grams	Diam. cm.	Height, cm.
<b>Short Beds</b>					
3	30	30.2	31.3	4.5	1.97
4	10	31.0	31.3	4.5	1.97
5	10	14.2	31.3	4.5	1.97
6	10	21.5	31.3	4.5	1.97
7	10	130	31.3	4.5	1.97
<b>Long Beds</b>					
1	120	30.5	384.5	4.2	26.0
2	120	58.1	362.6	4.2	25.6

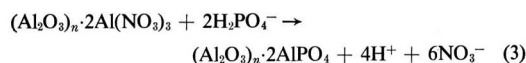
period of several days, they could not be monitored conveniently during the late night hours.

### Results and Discussion

Effluent samples from each run were collected and analyzed to account for their phosphate and nitrate concentrations and also for their pH values. In addition, random tests were also carried to establish the concentration of aluminum in the effluent. For a run in progress, these tests show that no measurable dissolved alumina were found in the effluent. However, for the initial phases of each run, the effluent was noted to contain fine particles of alumina that were elutriated from the bed. Once these fines were removed, the effluent remained clear and essentially free of dissolved alumina. For a typical example, the pH values and phosphate concentrations of the effluent for Run 6 [ $c_0 = 10$  mg.  $\text{PO}_4^{3-}$  per liter,  $F = 21.5$  cm.<sup>3</sup> per minute] are related to the total volumetric throughput in Figure 2.

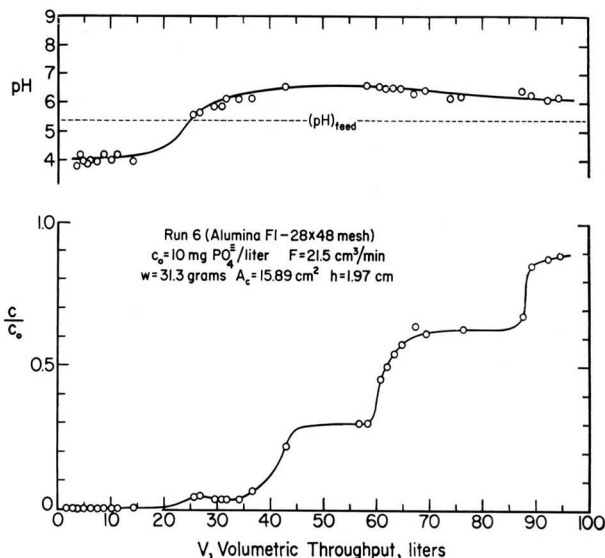
In this figure, the breakthrough curve for phosphate is characterized by the existence of three plateaus. This curve is asymptotic to  $c/c_0 = 0$  at the beginning and also approaches complete saturation to  $c/c_0 = 1$  at the end of the run. The initial complete removal of phosphate indicates that the advancing wave front of the reaction has not yet reached the top of the bed and the subsequent plateaus strongly infer the existence of specific reactions taking place on the surface of the alumina. The final asymptotic approach to saturation indicates that intraparticle diffusion becomes dominant and further complicates the mathematical description of the system. With increasing flow rates, the plateaus of the breakthrough curve become less apparent and eventually disappear at sufficiently high flow rates.

Values of pH of the effluent *vs.* volumetric throughput are also presented in Figure 2. Whereas the feed was measured to have a value of pH = 5.4, the initial effluent was more acidic with a value of pH  $\approx$  4.0. From these observations, the following initial reactions may occur on the surface of the alumina:



These results and their explanation are consistent with the findings of Churms (1966), who reports that the rate of phosphate exchange decreased with decreasing pH of the solution. Extending this argument, Sinha and Choudhury (1954) point

Figure 2. Relationships between  $c/c_0$  vs.  $V$  and pH vs.  $V$  for a typical short bed reactor run (Run 6)



out that phosphate removal by alumina becomes insignificant as the pH decreases from 3.00. This behavior can be explained by the fact that molecular  $\text{H}_3\text{PO}_4$  becomes the predominant form of the phosphate in solution at lower pH values. The reaction of Equation 3 indicates that at high pH values, the rate of phosphate removal should increase. This fact has been experimentally indicated by Valentine (1967) who showed better phosphate removals at the higher pH values. As already indicated, the existence of the phosphate as insoluble  $\text{AlPO}_4$  in acidic media has been verified by Cole and Jackson (1950). The pH values of the relationship of Figure 2 remain low as long as complete phosphate removal is indicated from the corresponding breakthrough curve. The appearance of phosphate in the effluent is accompanied by a corresponding increase in pH until a maximum pH value is reached which corresponds with the occurrence of the second plateau. The pH of the effluent then decreases with continuing throughput, passes through an inflection point which corresponds to the third plateau, and continues to decrease asymptotically to the value of the feed,  $\text{pH} = 5.4$ , as the breakthrough curve asymptotically approaches the saturated state of alumina.

No nitrate analyses were made on the samples of Run 6, because at the time the significance of the presence of this ion was not realized. However, the general trend of the nitrate ion concentration in the effluent was typical for all short beds provided with the same feed phosphate concentration. Figure 3 presents on semi-logarithmic coordinates, the nitrate depletion relationship for Run 4 ( $c_0 = 10 \text{ mg. PO}_4^{3-}$  per liter,  $F = 31.0 \text{ cm}^3$  per minute. This relationship indicates the existence of an initial abundant release in the effluent of nitrate ions which rapidly decreases through a sequence of plateaus to nitrate concentrations that could not be detected by the available method of analysis ( $0.1 \text{ mg. NO}_3^-$  per liter). These results indicate that the phosphate ions exchange with the nitrate ions present on the solid alumina and give rise to a strong inference that this exchange is chemical in nature. The chemical reaction postulated for this step is indicated in Equation 3.

Of the two long reactor studies, phosphate breakthrough curves and pH relationships resulting from the samples taken at each different level of Run 2 are presented in Figure 4. Each breakthrough curve is associated with a height up the

column ( $z = 0$ , influent). The breakthrough curve of the lowest section of the reactor reaches saturated conditions rapidly while the alumina at the top of the column remains free of phosphate. The advancing phosphate front in the alumina eventually reaches the top of the bed thus initiating a breakthrough curve at the effluent bed conditions. Corresponding pH relationships are also presented for each of these heights as shown in Figure 4. Each of the pH vs. throughput relationships is characterized with an initial acidic value and a maximum before these values begin to decrease and approach asymptotically the pH value of the feed. Furthermore, these maxima increase with height and exhibit an advancing displacement that relates to that indicated by

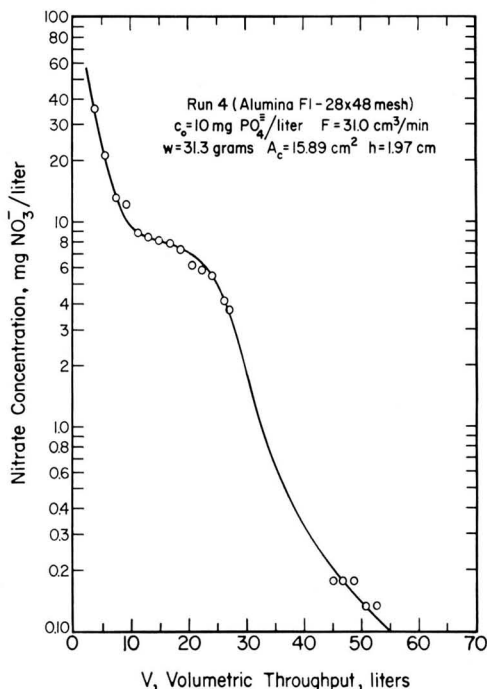


Figure 3. Relationship between concentration of nitrate in effluent stream and volumetric throughput (Run 4)

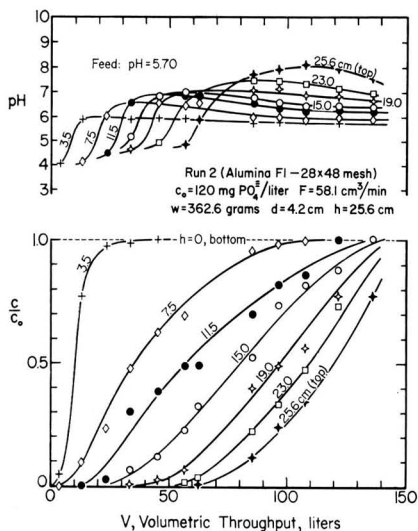
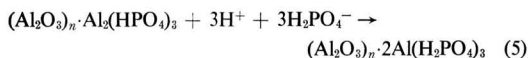
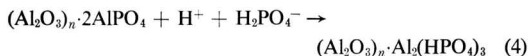


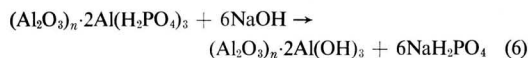
Figure 4. Relationships between  $c/c_0$  vs.  $V$  and pH vs.  $V$  at different bed heights of long reactor (Run 2)

the corresponding breakthrough curves. The information used to construct the relationships of Figures 2, 3, and 4 for Runs 2, 4, and 6 and for all the other runs is available from Neufeld (1968).

The fact that the solid alumina possesses the capability for removing phosphate when the effluent becomes free of nitrate ions and at the same time is accompanied by an increase in pH is consistent with the suggestions made by Churms (1966) who also witnessed the existence of plateaus in the uptake of a number of anions by activated alumina. These observations strongly suggest reformation reactions of the type:



The final product of Equation 5 represents the terminal state of alumina that must be regenerated before it can re-establish the capability of removing orthophosphate ions from solutions. The regeneration step which involves reaction with caustic (Yee, 1966) can be accounted for as follows:



The hydrated alumina,  $(\text{Al}_2\text{O}_3)_n \cdot 2\text{Al}(\text{OH})_3$ , can then be re-activated according to Equation 2 to repeat the cyclic process.

#### Data Treatment

A rigorous mathematical treatment involving the removal of constituents from fluids flowing through solid fixed beds becomes not only extremely complex, but also requires information concerning the properties of the solid and the fluid constituents that is difficult to obtain. For example, for the removal of water vapor from air using silica gel, Hougen and Marshall (1947) made a number of simplifications and assumed external mass transfer as the controlling mechanism to develop relationships that describe the breakthrough curves for the water vapor-silica gel system. To utilize their relationships, a number of system constants and parameters must be available. For the application of these relationships

to other systems, the model postulated for their development must also apply. Other examples of mathematical modeling which utilize a number of simplifications are presented in the literature (Amundson, 1950; Colwell and Dranoff, 1966; Crank, 1956; Tien and Thodos 1959).

The present experimental study does not readily lend itself to a rigorous mathematical analysis because of the combined effects of external mass transfer, internal diffusion, and the simultaneous changing chemical reactions that are associated with this system. Consequently, the approach adopted aims to utilize the information obtained in the present study to develop a correlative capability that is specific to the phosphate-alumina system. The method used to correlate these data should be applicable to other systems for which minimal experimental data are available.

Several attempts to describe the breakthrough curve mathematically have been made. The most effective method of correlation was found when values of  $c/c_0$  were plotted against the corresponding volumetric throughput using semi-probability paper. For Run 7, the breakthrough curve becomes essentially linear as shown in Figure 5, when  $c/c_0$  is plotted on the probability scale and volumetric throughput,  $V$ , on the rectilinear scale. Because of the high flow rate of Run 7, its breakthrough curve lacks the presence of the plateaus that become apparent with runs associated with low flow rates as shown for Run 6 in Figure 2. The linear relationship of Figure 5 can be expressed in general as follows:

$$\frac{c}{c_0} = \frac{1}{2} [1 + \text{erf}(mV + k)] \quad (7)$$

The breakthrough curves for the runs which exhibit prominent plateaus can be treated in the manner shown in Figure 5 to establish linear relationships which represent an overall compromise by averaging out the effects of these plateaus. The slopes,  $m$ , and intercepts,  $k$ , obtained from the results of the runs of this study are presented in Table II for the short bed heights. Error function values were obtained from the comprehensive tabulations of the National Bureau of Standards (1954). For these beds, the product  $c_0F$  has been related to the parameter  $m$  to establish on log-log coordinates the linear relationship of Figure 6. This relationship has been

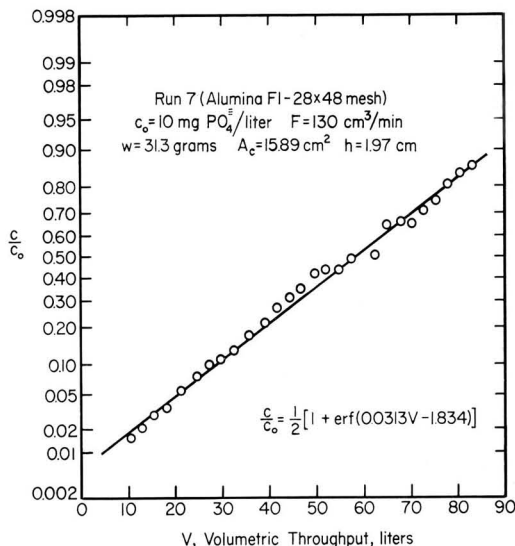


Figure 5. Linear relationship of breakthrough curve resulting when  $c/c_0$  is plotted against  $V$  on semiprobability coordinates (Run 7)

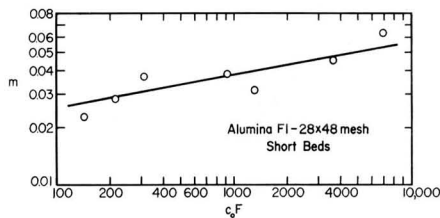


Figure 6. Relationship between slope,  $m$ , and  $c_0F$  for the short alumina beds of this study

developed for the short bed runs and therefore should be limited in application to heights comparable to these beds.

#### Evaluation of Capacity of Alumina.

The total phosphate transferred to the entire bed up to time  $\tau$  is  $Q$  and is,

$$Q = \frac{F}{1000} \int_0^\tau (c_0 - c) d\tau \quad (8)$$

Since for a constant flow rate,  $F$ , the volumetric throughput is  $V = F\tau/1000$ , it follows that,

$$Q = \int_0^{V_f} (c_0 - c) dV = c_0 \int_0^{V_f} \left[ 1 - \frac{c}{c_0} \right] dV \quad (9)$$

where  $V_f$  represents some arbitrary final volumetric throughput through the bed. Substituting Equation 7 into Equation 9 and noting that

$$\int_0^x \operatorname{erf} x dx = x \operatorname{erf} x + \frac{e^{-x^2}}{\sqrt{\pi}} \quad (10)$$

it follows upon a change of the variable of Equation 10,  $x = mV + k$ , that

$$Q = \frac{c_0}{2} \left\{ V - \frac{1}{m} \left[ (mV + k) \operatorname{erf}(mV + k) + \frac{e^{-(mV+k)^2}}{\sqrt{\pi}} \right] \right\}_{0}^{V_f} \quad (11)$$

Upon letting  $V_f \rightarrow \infty$ , it follows that  $\operatorname{erf}(mV_f + k) \rightarrow 1$  and  $e^{-(mV_f+k)^2} \rightarrow 0$ , and therefore,

$$Q = \frac{c_0}{2} \frac{k}{m} \left[ -1 + \operatorname{erf} k + \frac{e^{-k^2}}{k\sqrt{\pi}} \right] \quad (12)$$

Using Equation 7 and noting that when  $c/c_0 = 0.5$ ,  $V_{0.50} = -k/m$ , it then follows that Equation 12 can be expressed in terms of the parameters  $k$  and  $m$  and the volumetric throughput resulting from the data when  $c/c_0 = 0.50$ . Thus, by letting  $Q = wq$ , it follows that the concentration of the solute in the solid phase becomes

$$q = \frac{c_0}{w} V_{0.50} \left[ \frac{1 - \operatorname{erf} k}{2} - \frac{e^{-k^2}}{2k\sqrt{\pi}} \right] \quad (13)$$

It should be noted that  $q$  represents an equilibrium value existing in the solid phase when the liquid phase concentration in contact with it is  $c_0$ . Equation parameters  $m$  and  $k$  presented in Table II were used to evaluate for each bed the capacity and the corresponding equilibrium value  $q$ . The resulting values of  $q$  for each run are summarized with their corresponding values of  $c_0$  in Table III. In these capacity calculations, the total weight of each bed was used along with the corresponding values of  $m$  and  $k$  resulting from their respective effluents. For Runs 1 and 2, the averaged value,

Table II. Parameters  $m$  and  $k$  for Equation 7 for Short Bed Heights

Run	$c_0F$	$m$	$k$
1 <sup>a</sup>	3680	0.0457	-1.823
2 <sup>a</sup>	6970	0.0647	-0.408
3	905	0.0384	-1.368
4	310	0.0376	-2.512
5	142	0.0228	-1.428
6	215	0.0288	-1.861
7	1300	0.0313	-1.834

<sup>a</sup> Breakthrough curve taken at height = 3.5 cm.

Table III. Equilibrium Values Resulting from Capacity Calculations

Run	$c_0$ Mg. $\text{PO}_4^{3-}$ per Liter	$q$ Mg. $\text{PO}_4^{3-}$ per Gram of Alumina
1	120	40.39
2	120	40.03
3	30	33.3
4	10	21.1
5	10	20.6
6	10	20.6
7	10	18.75

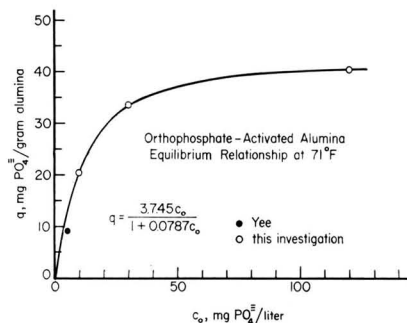


Figure 7. Equilibrium relationship for orthophosphate in solution and on solid alumina at 71°F.

$q = 1/2 [40.39 + 40.03] = 40.21$  mg.  $\text{PO}_4^{3-}$  per gram applies to  $c_0 = 120$  mg.  $\text{PO}_4^{3-}$  per liter. Also, the average value for Runs 4, 5, 6, and 7,  $q = 1/4 [21.1 + 20.06 + 20.6 + 18.75] = 20.26$  mg.  $\text{PO}_4^{3-}$  per gram applies to  $c_0 = 10$  mg.  $\text{PO}_4^{3-}$  per liter. These averaged values, along with  $q = 33.3$  mg.  $\text{PO}_4^{3-}$  per gram and  $c_0 = 30$  mg.  $\text{PO}_4^{3-}$  per liter for Run 3 have been used to establish the equilibrium relationship presented in Figure 7. These equilibrium values properly fit a Langmuir type isotherm for  $c_0 \leq 120$  mg.  $\text{PO}_4^{3-}$  per liter and establish the relationship

$$q = \frac{3.745c_0}{1 + 0.0787c_0}$$

The single value of Yee (1966) at  $c_0 = 5$  mg.  $\text{PO}_4^{3-}$  per liter and  $q = 9$  mg.  $\text{PO}_4^{3-}$  per gram is included for comparison in Figure 7.

#### Nomenclature

$A_c$  = cross sectional area of reactor, cm.<sup>2</sup>  
 $c$  = concentration of orthophosphate in solution, mg.  $\text{PO}_4^{3-}$  per liter  
 $c_0$  = concentration of orthophosphate in feed solution, mg.  $\text{PO}_4^{3-}$  per liter

$d$  = diameter of reactor, cm.  
 $e$  = constant, 2.71828  
 $F$  = flow rate of solution, cm.<sup>3</sup> per minute  
 $h$  = height of fixed bed, cm.  
 $k$  = constant, Equation 7  
 $m$  = constant, Equation 7  
 $q$  = equilibrium concentration of solute in solid phase, mg. PO<sub>4</sub><sup>3-</sup> per gram  
 $Q$  = quantity of solute in solid phase, mg.  
 $V$  = volumetric throughput, liters  
 $V_f$  = final volumetric throughput, liters  
 $w$  = weight of fixed bed, grams  
 $x$  = variable

#### Greek Letters

$\pi$  = constant, 3.1416  
 $\tau$  = time

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## Fractionation of Bomb-Produced Rare-Earth Nuclides in the Atmosphere

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■ The phenomenon of atmospheric fractionation of fission products occurs on a world-wide scale when fresh debris from a nuclear explosion travels eastward and circles the earth. Among the rare-earth radionuclides, <sup>91</sup>Y and <sup>141</sup>Ce were often depleted relative to other rare earths in fallout samples collected several days after the Chinese nuclear detonation of December 24, 1967. This is due to the existence of gaseous precursors in the mass 91 and 141 chains. Pronounced fractionation phenomena were also observed for fission products at mass numbers A = 89 (Sr), A = 131 (I), and A = 140 (Ba).

The fact that fresh debris from a single nuclear explosion travels eastward and circles the earth within a few weeks has recently been reported (Cooper and Kuroda, 1966; Kuroda, Miyake, *et al.*, 1965; Thein and Kuroda, 1967). Fission products are highly fractionated in the so-called "hot" particles (Baugh, Yoshikawa, *et al.*, 1967; Clark Yoshikawa, *et al.*, 1967; Rao, Yoshikawa, *et al.*, 1966). Since large and small fallout particles are expected to travel

at different velocities in the atmosphere, the fallout observed at different times and at different localities of the earth should reflect the particle size distribution in time and space. Thus, the effects of atmospheric fractionation of nuclear debris should be observable on a global scale. Knowledge of the global atmospheric fractionation of nuclear debris is essential in the understanding of the process of fallout from nuclear weapons tests.

The atmospheric fractionation phenomena in local or close-in fallout processes have been studied extensively by many investigators (Klement, 1965). The studies on world-wide fractionation phenomena are more difficult and require a single isolated nuclear test explosion so that it is possible to trace the movement of the fresh debris for a sufficiently long period, while the debris circles the earth at least once. It is also essential to make sure that the observed fractionation phenomena are not caused by secondary processes, such as fractionation due to incomplete dissolution of the samples. In the present study, we have measured a number of rare-earth nuclides, as well as Sr, Ba, Te, and I isotopes in rain collected at Fayetteville, Ark. The rare-earth nuclides are particularly suited for this type of investigation, because they can not be easily fractionated under laboratory conditions.

#### Experimental

For the radiochemical separation of the rare-earth nuclides from rain, 8 to 24 liters of rain samples were taken in each case. About 20 mg. each of Y, Ce, Pr, Nd, Sm, and Eu nitrates

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**Table I. Fission Products in Rain at Fayetteville, Ark.**

Nuclide	Half-life	Concentrations in Rain (p.c./l.) <sup>a</sup>				
		12-30-67	1-1-68	1-2-68	1-5-68	1-8-68
<sup>91</sup> Y	59d <sup>b</sup>	92 ± 7	96 ± 8	135 ± 9	42 ± 6	19 ± 2
<sup>141</sup> Ce	32.5d	115 ± 12	230 ± 30	230 ± 30	83 ± 8	13 ± 2
<sup>144</sup> Ce	285d	44 ± 4	66 ± 7	78 ± 8	31 ± 3	12 ± 2
<sup>143</sup> Pr	13.7d	400 ± 30	880 ± 60	1040 ± 80	220 ± 20	36 ± 3
<sup>147</sup> Nd	11.1d	198 ± 18	340 ± 30	360 ± 20	88 ± 6	14.0 ± 1.8
<sup>147</sup> Pm	2.6y	4.8 ± 0.6	12.2 ± 1.1	17.1 ± 1.4	7.4 ± 0.6	12.0 ± 1.4
<sup>149</sup> Pm	53h	—	100 ± 20	—	—	—
<sup>151</sup> Sm	90y	2.5 ± 0.3	1.3 ± 0.3	—	1.6 ± 0.2	—
<sup>152</sup> Sm	47h	—	22 ± 5	—	—	—
<sup>155</sup> Eu	1.8y	—	—	4.5 ± 0.5	0.8 ± 0.1	—
<sup>156</sup> Eu	15.2d	3.8 ± 0.5	5.6 ± 0.8	—	—	—
<sup>89</sup> Sr	50.6d	24.8 ± 1.7	34 ± 3	65 ± 6	147 ± 10	46 ± 2
<sup>90</sup> Sr	28.8y	4.52 ± 0.16	3.08 ± 0.13	4.8 ± 0.5	6.5 ± 1.2	3.43 ± 0.52
<sup>115m</sup> Cd	43d	—	0.50 ± 0.20	0.67 ± 0.13	0.45 ± 0.15	—
<sup>129m</sup> Te	34d	10.6 ± 0.3	55.0 ± 9.0	38 ± 4	9.7 ± 0.5	—
<sup>131</sup> I	8.05d	30 ± 3	54 ± 5	12.6 ± 1.3	5.1 ± 0.5	1.9 ± 0.5
<sup>132</sup> Te	78h	13 ± 2	35 ± 4	5.0 ± 0.5	—	—
<sup>140</sup> Ba	12.8d	180 ± 20	138 ± 14	367 ± 37	263 ± 26	154 ± 15

<sup>a</sup> As of the date of rainfall.  
<sup>b</sup> y = years, d = days, h = hours.

were added to the sample. The solution was then evaporated to about 20 ml., transferred to a Teflon beaker, and further evaporated to a small volume. A 20-ml. portion of HNO<sub>3</sub> was added to the solution and again evaporated to a small volume. The solution was then treated with 20 ml. of fuming HNO<sub>3</sub>, 10 ml. of conc. HClO<sub>4</sub> and 10 ml. of conc. HF, and

were evaporated until the perchloric acid fumed. The treatment with HClO<sub>4</sub> + HNO<sub>3</sub> + HF was repeated and the rare-earth fluorides were precipitated in a lusteroid tube.

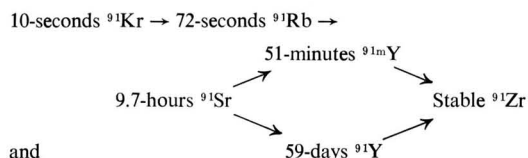
The rare-earths as a group were purified from other fission products by the method of Stevenson and Nervik (1961). The individual rare-earth nuclides were separated by the use of 50W-X8 200- to 400-mesh cation-exchange resin and the concentration gradient-elution technique originally described by Wolfsberg (1962).

Strontium, barium, and iodine isotopes were purified by the methods employed in earlier studies (Beck and Kuroda, 1966; Cooper and Kuroda, 1966; Reynolds, Swindle, *et al.*, 1967). Tellurium was isolated and purified by the method of Goeckermann, as reported by Meinke (1964). Tin was determined by the method of Hoffman (Hoffman, Lawrence, *et al.*, 1964). Tracerlab CE-14SL Low Background Beta Counters were used for the radioactivity measurements. The backgrounds of the counters were about 1.5 c.p.m.

*Results and Discussion*

The experimental results are shown in Table I. The concentrations of the fission products with half-lives shorter than that of <sup>91</sup>Y (59 days) are expressed in terms of the number of atoms per liter as of the date of nuclear explosion (December 24, 1967) and are plotted in Figure 1 *a-e*.

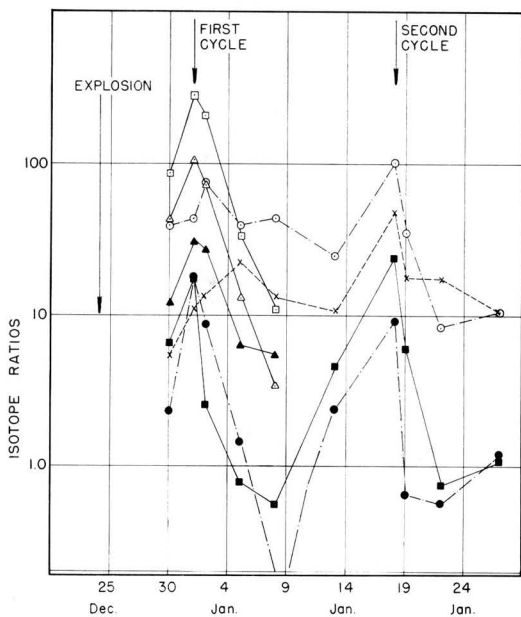
Rare-earth nuclides (except <sup>91</sup>Y and <sup>141</sup>Ce), Te, Sn, and Cd isotopes define the general shape of the mass-yield curve for neutron-induced fission of <sup>235</sup>U. The fact that the concentrations of <sup>91</sup>Y and <sup>141</sup>Ce are often appreciably lower than expected from the mass-yield curve can be understood as due to the loss of gaseous precursors at the time of fallout particle formation, shortly after the nuclear detonation. The mass 91 and 141 decay chains are (Hyde, 1964):



**Table II. Daily Variation of Large and Small Fallout Particles in the Ground-Level Air at Fayetteville, Ark.**

Date	Number of Particles in 3300 m <sup>3</sup> of Air	
	Large (>2-3 μ)	Small (<1-2 μ)
12-28-67	1	19
12-29-67	2	17
12-30-67	11	34
12-31-67	0	12
1- 1-68	4	26
1- 2-68	2	33
1- 3-68	3	37
1- 4-68	1	9
1- 5-68	1	35
1- 6-68	0	39
1- 7-68	2	31
1- 8-68	7	120
1- 9-68	0	56
1-10-68	0	48
1-11-68	2	19
1-12-68	4	80
1-13-68	5	38
1-14-68	1	28
1-15-68	2	53
1-16-68	0	18
1-17-68	2	104
1-18-68	5	110
1-19-68	3	105
1-20-68	2	307
1-21-68	2	206
1-22-68	3	210
1-23-68	1	136
1-24-68	2	67





**Figure 2.** Variations of the ratios of short-lived fission products to  $^{90}\text{Sr}$  in rain samples collected at Fayetteville, Ark., after the December 24, 1967, Chinese nuclear explosion

The ratios are expressed in terms of curie/curie as of the dates of rainfalls



## Vapor Density of Dieldrin

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■ Vapor density associated with solid-phase dieldrin (HEOD, 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene) and dieldrin-soil mixtures, measured by a gas-saturation technique, was three to 12 times greater than predicted from published vapor pressure values. The measured vapor densities at 20, 30, and 40° C. were 54, 202, and 676 ng. of HEOD per liter, respectively. The vapor density of HEOD in three dry dieldrin materials was the same as that of HEOD plus water. The vapor density of HEOD in soil at 100 p.p.m. was the same as that of HEOD without soil, but at 10 p.p.m. the vapor density in soil was reduced approximately 80%. The heat of vaporization of HEOD with or without soil was 23.6 kcal. per mole. The data indicate that the so-called "codistillation" phenomenon is not due to an increased vapor density in the presence of evaporating water and that loss of water is not required to attain maximum vapor density of HEOD, either in soil or over HEOD-water mixtures.

Considerable evidence (Bowman, Schechter, *et al.*, 1965; Edwards, 1966; Harris and Lichtenstein, 1961) indicated that volatilization from the soil surface may be an important pathway for loss of dieldrin and other relatively per-

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sistent organochlorine insecticides. Acree (1963), Bowman, Acree, *et al.* (1959, 1964), and Bowman, Schechter, *et al.*, (1965) reported that loss of water contributed to the volatilization of DDT and other insecticides by an apparent "codistillation" process. They implied that loss of water was necessary for significant volatilization to occur from water or soil surfaces.

A project was recently initiated to evaluate factors affecting vapor-phase movement and volatilization losses of organochlorine compounds in soils. The attainment of this objective required the determination of factors affecting the relationship between the solid-phase concentration in soils and vapor density. Dieldrin vapor density in association with solid-phase dieldrin and dieldrin-soil mixtures is reported here. The results are compared with vapor densities calculated from vapor pressure values reported by Porter (1964), and implications to HEOD vapor species and rates of volatilization are discussed.

## Experimental

Vapor density of dieldrin (HEOD) in association with solid-phase dieldrin and dieldrin-soil mixtures was determined by a gas saturation method using high-purity dry nitrogen as a carrier gas in apparatus similar to that shown in Figure 1. In the gas saturation method a current of inert gas is passed through

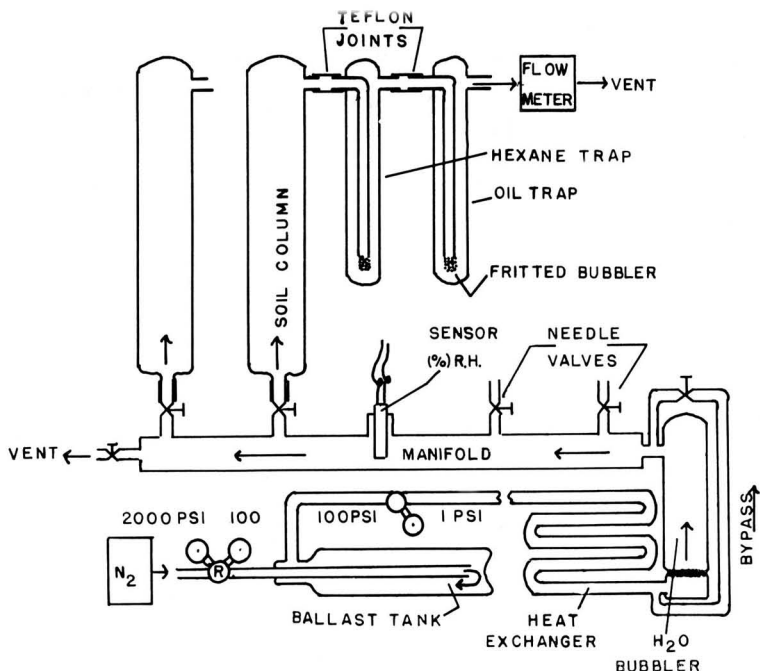


Figure 1. Schematic diagram of flow system used to determine dieldrin vapor density by the gas saturation method

or over the material at a sufficiently slow rate to ensure equilibrium saturation (Thompson, 1963). The entire apparatus, except the nitrogen supply tank, the high-pressure regulator, and the bubble-flow meter, were inside a constant temperature incubator. The assembly included a heat exchanger to bring the temperature of the  $N_2$  gas to the temperature of the incubator, a water bubble-chamber with bypass to adjust the humidity of the  $N_2$ , and a pressure regulator to maintain a constant pressure of 1 p.s.i. in the manifold. A relative humidity and temperature sensor was installed in the manifold and the flow of gas through the columns was regulated by needle valves. The humidity could be accurately controlled by adjusting the proportion of the nitrogen passing through the humidifying chamber and the amount of gas flowing out the relief valve at the end of the manifold.

The 6- × 43-cm. dieldrin-saturating columns were made from medium-wall borosilicate glass tubing capped with 60/50 Teflon joints. For soil-dieldrin mixtures the columns were mounted vertically as shown in Figure 1. For measuring vapor density of HEOD without soil the columns were mounted horizontally with the HEOD placed either in the bottom or coated on the sides of the columns. Vapor phase HEOD was removed from the slowly flowing  $N_2$  gas stream in hexane-oil traps consisting of two 250-ml. gas-washing bottles connected in series with Teflon tubing. The first trap contained 150 ml. of hexane which effectively removed all the HEOD. The second trap contained 150 ml. of transmission oil which trapped the hexane volatilized from trap 1. This was required to maintain a fairly constant liquid head and to prevent undue interference of hexane with the flow measurement in the bubble-flow meter.

To calculate vapor density in weight per unit volume of gas passing through the saturator, it was necessary to correct the measured volumes for pressure and temperature differences and for the net volume of hexane added to the nitrogen stream between the saturator and the flow meter. The traps were weighed to determine the amount of hexane passing through the flow meter. The flow meter was at ambient temperature; the saturator was at controlled temperatures and exposed to

slightly higher pressures due to resistance to flow through the fritted bubblers and the liquid head of the trapping medium. A mercury manometer was used to establish the pressure within the saturator. The value for the volume of  $N_2$  passing through the saturator was established from the measured volume by assuming that Dalton's law was valid for the hexane vapor lost to the gas stream and by correcting to the saturator temperature and pressure using the ideal gas laws. Additional information concerning these calculations can be found in Thompson (1963).

Recrystallized dieldrin, 99% HEOD (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene), obtained from Shell Chemical Co. was used as the dieldrin material in all studies except for some comparative measurements made with Shell Technical Dieldrin and analytical-grade dieldrin obtained from the Polyscience Corp. For vapor density of HEOD only, 1 gram of dieldrin was placed in the bottom of the saturator chamber. To determine the effect of water on vapor density of HEOD, measurements were made with 100 ml. of water sufficient to cover the dieldrin partially, in the bottom of the saturator.

The Gila silt loam used in these studies is a desert soil containing approximately 18.4% clay, 0.6 organic matter, with a surface area of approximately 90 sq. meters per gram and an exchange capacity of 18 meq. per 100 grams. The clay fraction is predominantly montmorillonite with lesser amounts of mica, quartz, and feldspars. In preparing columns, the soil was first autoclaved and exposed to moist air for several days before adding dieldrin. Sufficient dieldrin in 100 ml. of acetone for 10 or 100 p.p.m. HEOD was added to the soil and the soil thoroughly mixed. The soil was aerated with moist air to remove the acetone, then adjusted to 3.9% water content by adding a predetermined amount of water with an atomizer, mixing thoroughly, and equilibrating at 94% relative humidity. After the columns were packed with approximately 900 grams of treated soil, they were placed in an incubator at 30° C. for 30 days before measurements were initiated.

In the gas saturation method, when equilibrium between the

gas and solid phase is obtained, the amount of vapor trapped per unit time should vary linearly with the flow rate of the gas. In the present experiments, the flow rate of the N<sub>2</sub> gas was varied between 1 and 300 ml. per minute with HEOD only in the saturator, and between 1.7 and 12.6 ml. per minute with the soil columns. Within these ranges of flow rates the HEOD vapor densities were independent of flow rate within the experimental error of the method. This made it unnecessary to control rigidly the flow rate, and only required monitoring it frequently enough to establish the total volume of gas flowing through the saturator during each run. The nitrogen gas flow rates remained essentially constant within each individual run, but rates from 3 to 6 ml. per minute were generally used to provide a total flow through the saturator of from 10 to 80 liters, depending upon the expected concentration of dieldrin in the N<sub>2</sub> gas and the amount of dieldrin required for quantitative estimation. The HEOD content of the hexane was determined, after appropriate concentration in a Kuderna-Danish concentrator, by gas-liquid chromatography using a Beckman GC-5 equipped with a nonradioactive electron-capture detector. From three to nine measurements were made on each set of columns at each of three temperatures, 20, 30, and 40° C.

The possibility of entrainment and surface creep as a factor influencing measurements was investigated by measuring vapor density with and without a 4-foot coil of Teflon tubing between the saturator and hexane trap. The insertion of the 4-foot coil of tubing did not significantly affect measured vapor density values and was not used for the data reported herein.

### Results and Discussion

The vapor density and calculated vapor pressures of dieldrin (HEOD) with and without water are shown in Table I. The vapor density in association with dry HEOD was the same as that associated with HEOD plus water, indicating that the presence of water or evaporating water had no appreciable influence on the vapor density, or potential vaporization rate. Vapor density of HEOD in dry Shell Technical dieldrin and analytical grade dieldrin from the Polyscience Corp. was the same as that reported in Table I for dry HEOD at comparable temperatures.

Dieldrin vapor density increased markedly with temperature. The apparent vapor pressures were calculated from the vapor density,  $W/V$ , with the equation:

$$P = (W/V)(RT/M) \quad (1)$$

where  $R$  is the molar gas constant,  $T$  the absolute temperature, and  $M$  the molecular weight of HEOD assuming a monomer gaseous species.

Combining all "wet" and "dry" HEOD measurements resulted in a mean vapor density of 54, 202, and 676 ng. HEOD per liter equivalent to an apparent vapor pressure of  $2.6 \times 10^{-6}$ ,  $10.0 \times 10^{-6}$ , and  $34.7 \times 10^{-6}$  mm. of Hg at 20, 30, and 40° C., respectively. The following equation, graphically shown in Figure 2, relates this apparent vapor pressure to temperature:

$$\text{Log}_{10}P = 12.07 - (5178/T) \quad (2)$$

Porter (1964) reported the vapor pressure of HEOD to be  $0.78 \times 10^{-6}$ ,  $1.43 \times 10^{-6}$ , and  $2.74 \times 10^{-6}$  mm. of Hg at 20, 30, and 40° C., respectively. These values were obtained using an effusion technique (Porter, 1968). The measured vapor densities are from three to 12 times greater than would be predicted from Porter's "static" vapor pressure values.

The vapor density and calculated vapor pressure of HEOD in Gila silt loam soil in relation to temperature and concentration of HEOD are shown in Table II. For these measurements the soil-water content was 3.9% which, in Gila silt loam, is equivalent to 94% relative humidity, or approximately 90 bars matric suction. The humidity of the nitrogen carrier gas was in equilibrium with this moisture content, which resulted in no net loss of water from the soil column during the measurements. At 100 p.p.m. of HEOD in soil the vapor density was the same as that of HEOD without soil. Thus, a saturated vapor density was attained in soil, and Equation 2 adequately describes the linear relationship between  $\text{Log } P$  and  $1/T$  for this concentration. At 10 p.p.m. of HEOD, the vapor density was approximately 20% as great as that of HEOD without soil. Equation 3 expresses the linear relationship between  $\text{Log } P$  and  $1/T$  for 10 p.p.m. of HEOD:

$$\text{Log}_{10}P = 11.33 - (5170/T) \quad (3)$$

This relationship is graphically shown in Figure 2.

According to one form of the Clausius-Clapeyron equation, the slope ( $m$ ) of the line, when  $\text{Log}_{10}P$  is plotted vs.  $1/T$  is related to heats of vaporization by the equation:

$$\Delta H_v = -2.303Rm \quad (4)$$

where  $\Delta H_v$  is heat of vaporization in calories per mole when  $R$  is in calories per mole per degree. Since the slopes for ad-

Table I. Vapor Density and Calculated Vapor Pressures of Dieldrin (HEOD) with and without Water

	Temp., °C.	Vapor Density, Ng./L.	Vapor Pressure, <sup>a</sup> Mm. Hg $\times 10^{-6}$
HEOD (wet) <sup>b</sup>	20	52 $\pm$ 5 <sup>c</sup>	2.6
	30	199 $\pm$ 9	9.9
	40	685 $\pm$ 38	35.1
HEOD (dry)	20	59 $\pm$ 5	2.8
	30	205 $\pm$ 19	10.1
	40	661 $\pm$ 16	33.9

<sup>a</sup> Calculated from vapor density,  $W/V$  with the equation:  $P = \frac{W}{V} \cdot \frac{RT}{M}$  using 381 as the molecular weight ( $M$ ) of the gaseous species.

<sup>b</sup> With 100 ml. of water in the saturation chamber.

<sup>c</sup> The 95% confidence limit or  $2 \times$  standard error of the mean calculated for each series of runs.

Table II. Vapor Density and Calculated Vapor Pressure of HEOD in Gila Silt Loam Soil

HEOD Concn., P.P.M.	Temp., °C.	Vapor Density, Ng./L.	Vapor Pressure Mm Hg $\times 10^{-6}$
100	20	45 $\pm$ 3 <sup>a</sup>	2.2
	30	205 $\pm$ 19	10.2
	40	690 $\pm$ 17	35.4
10	20	10 $\pm$ 0.6	0.5
	30	37 $\pm$ 3	1.9
	40	130 $\pm$ 8	6.7

<sup>a</sup> The 95% confidence limit or  $2 \times$  standard error of the mean calculated for each series of runs.

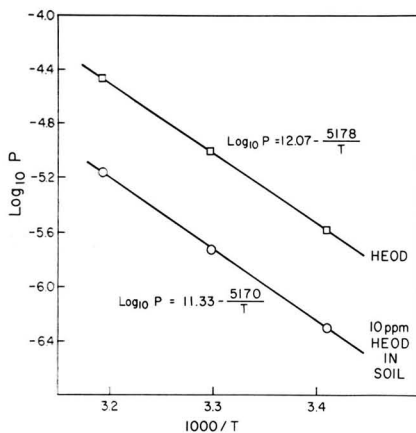


Figure 2. The relationship between apparent vapor pressure of HEOD and temperature

sorbed and unadsorbed HEOD are similar, heats of vaporization are also similar. Heats of vaporization for unadsorbed HEOD and for 10 p.p.m. of HEOD in soil, calculated with Equation 4, were 23.6 kcal. per mole.

Other relevant thermodynamic quantities were calculated from the change in vapor pressure with temperature using the following equations from Oster and Low's (1963) treatment of clay-adsorbed water:

$$\Delta H \text{ or } \bar{H}_a - H^0 = (\bar{H}_a - \bar{H}_v) - (H^0 - \bar{H}_v) = (\Delta H_v)^0 - (\Delta H_v)_a \quad (5)$$

$$\Delta F \text{ or } \bar{F}_a - F^0 = RT \ln (P_a/P^0) \quad (6)$$

$$\Delta S \text{ or } \bar{S}_a - S^0 = [(\bar{H}_a - H^0) - (\bar{F}_a - F^0)]/T \quad (7)$$

where  $\Delta H_v$  is the heat of vaporization of adsorbed or unadsorbed HEOD;  $H$ ,  $F$ , and  $S$  are the heat content, free energy, and entropy of the HEOD, respectively;  $R$  is the molar gas constant;  $T$  the absolute temperature,  $P$  is the vapor pressure of HEOD; the bars over the symbols designate partial molar quantities; the subscripts "a" and "v" refer to the adsorbed and vapor states; and the zero superscript refers to the standard state HEOD without soil at 30° C.

The change in free energy,  $\Delta F$ , on adsorption of HEOD at 10 p.p.m., calculated from the ratio of the vapor pressure of HEOD only *vs.* soil at 10 p.p.m. of HEOD, was -1000 calories per mole at 30° C. The change in entropy,  $\Delta S$ , due to adsorption of the HEOD at 10 p.p.m. calculated with Equation 7 using heats of vaporization calculated from the linear plot of  $\text{Log}_{10} P$  *vs.*  $1/T$  was +3.43 calories per degree per mole at 30° C. The entropy of the adsorbed state at 10 p.p.m. of HEOD was greater than the entropy of solid-state HEOD. Since a gain in entropy is related to a decrease in order, this would imply that adsorbed HEOD at 10 p.p.m. was less ordered than solid-state HEOD or HEOD at 100 p.p.m. in soil. A decrease in entropy on adsorption is usually observed as reported by Oster and Low (1963) for adsorption of water on clays.

The discrepancy in vapor density between that calculated from Porter's data and measured in our experiments could be

due to insufficient saturation of the atmosphere in the effusion measurements reported by Porter, or to association of HEOD molecules in the vapor state in the measurements reported herein using the gas saturation technique. To explain the discrepancy entirely on the latter basis would require molecular groupings of increasing size as the temperature increased, and assuming that the molecules were leaving the dieltrin surface as groups of molecules rather than as monomers. According to Lewis and Randall (1961), the mean molecular weight of the vapor species may be determined by comparing measured vapor densities with densities calculated from static vapor pressure values. Based on this comparison, the average number of molecules per associated group, or polymer size, needed to explain the discrepancy between measured and calculated vapor densities is 3.4, 7.0, and 12.7 at 20, 30, and 40° C., respectively. Groups of 3, 7, and 12 HEOD molecules would be approximately 12, 16, and 20 Å. in diameter, respectively. Bowman, Acree, *et al.* (1960) concluded that DDT was present in water as finely divided suspended particles rather than as a true solution of individual molecules. Dieltrin probably behaves similarly in water, and it is logical that the smaller groups of molecules may escape into the atmosphere from the air-water interface.

The increase in entropy on adsorption indicates that possibly the interaction with soil resulted in less association between molecules in the vapor state, probably due to breakdown of the HEOD into smaller molecular groups or into individual molecules on the surface of the soil clays. The altering of vapor species by interaction with various solids has been reported previously (Lewis and Randall, 1961).

The fact that the vapor density and heat of vaporization of dieltrin applied to soil at 100 p.p.m. is the same as pure HEOD indicates that the adsorption forces between dieltrin and soil are quite weak and probably the dieltrin is present as globules or is adsorbed at the air-water interface. When applied at rates of 100 p.p.m. or greater to a soil with even a small amount of water, dieltrin can vaporize initially from soil as easily as from pure HEOD; therefore, surface applications of dieltrin and probably other similar organochlorine insecticides will volatilize rapidly from the soil until the concentration at the surface falls somewhat below 100 p.p.m. To illustrate potential vaporization rates, at 30° C. and a flow rate of 300 ml. per minute, dieltrin vaporized from the dieltrin-water surface in the saturation chamber at the rate of approximately 0.35 ng. per sq. cm. per minute, or approximately 0.05 pound per acre per day. At this flow rate the air flow across the water surface in the relatively large saturation chamber was only 15 cm. per minute, or less than 0.006 m.p.h. At air-flow rates encountered under field conditions, the potential rate of volatilization would be considerably higher.

The fact that water covering the HEOD in the saturation chamber did not affect the vapor density and that relatively low concentrations in soil resulted in the same vapor density as the pure material while not losing moisture, would indicate that the evaporation of water does not contribute to increased vapor density, or "potential volatility." The reported discrepancies between volatilization rates from water surfaces and those predicted from vapor pressure measurements may be partly due to the presence of much higher vapor densities than predicted from vapor pressure measurements based on effusion or other techniques not involving direct measurements of concentration of the material in the vapor phase.

Studies continue on the concentration in soil at which vapor density falls below the saturation value, and on factors affecting actual volatilization rates, such as soil-water content, temperature, and soil characteristics.

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## COMMUNICATION

### Apparatus for Continuous Solids-Liquid Separation

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■ The apparatus, which allows high filtration with a Millipore filter on a long-term basis, consists of a Plexiglas box built around a standard Millipore filter holder. The entrance port in the box contains a nozzle which increases the velocity of the incoming solution and directs it into a tangential flow pattern, simultaneously supplying the mixture to be filtered as well as washing the filter clean of separated solids. Filtrate containing only particles smaller than 0.45 micron in diameter can be recovered continuously at rate of 100 ml. per hour. Alternating use of two of the units in parallel allows continuous removal.

The continuous separation of solids from liquids, with recovery of both fluid and thickened solids, is frequently required in chemical and biologic processes. As a unit process on a large scale, the separation can be performed by many commercial units and techniques (Marshall, Mately *et al.*, 1966) which are designed to separate volumes at greater than 60 liters per hour effectively (at correspondingly substantial capital investments). In small pilot-plant or bench-scale studies, however, where volumes may only be a few liters a day, the problem of effective separation becomes acute.

There are many "batch" operations for separating small quantities of solid-liquid slurries or mixtures (such as centrifugation, gravity filtration, and vacuum filtration). However, no continuous separating system is currently available on the market which can be readily integrated into an existing process and allow further processing of the resulting liquid and thickened solids.

A small-scale continuous separation system was needed in this laboratory for use on a high-solids activated sludge unit (suspended solids levels approaching 20 grams per liter). Activated sludge is one of several candidate processes for degrading human wastes into non-noxious compounds which may be used to support plant life in a bioregenerative life-

support system. In preliminary studies with our high-solids sludge unit, separation of the effluent from the biomass by flocculation and gravity sedimentation proved unsatisfactory because the bacterial mass concentrations, being about 10 times as great as conventional levels, proved to be too voluminous and its settling properties rapidly deteriorated. A separator was desired which would remove the effluent from the sludge and return the thickened solids to the culture vessel immediately to have a closed ecosystem.

A review of the literature revealed no apparatus which met our specifications, namely, one that was compact, inexpensive, had no moving parts, and could be easily serviced. The Millipore Filter Corp. has described a novel application of the Millipore filter (thin cellulose porous membranes using vacuum as the driving force to attain solids retention down to 0.45 micron in size) (1960): the use of a Microweb filter (large flexible sheets of Millipore filter material) supported by mesh on a spinning drum. When the drum is evacuated, clarified effluent is drawn through the filter and the filter is kept clean by the high centrifugal force applied to the collected material on the spinning drum (Snuggs, 1967). While this system appeared capable of long-term operation with continuous solids separation, the rotational characteristics (with its associated vacuum sealing problems) appeared undesirable. Hence, the apparatus described below was developed to accomplish the same purpose in a way to make a compact, inexpensive unit without the problem of rotary vacuum seals.

#### Description

Figure 1 presents the apparatus with the component parts identified (Ryan, 1967). It is constructed of Plexiglas, 1.3-cm. thick, built around a standard Millipore filter holder in the form of a box 8.9- × 12.7- × 9.2-cm. The box has stainless steel entrance and exit ports both having a diameter of 1.3 cm. The entrance port has a nozzle (measuring 2.54- × 0.16-cm.) that increases the velocity of the incoming solution and directs it into a tangential flow pattern, simultaneously supplying the new mixture to be filtered and washing the filter clean of any separated material clogged on its surface as a result of the vacuum filtration process. The Millipore filter paper is held in

<sup>1</sup>Present address, 824th USAF Dispensary, APO San Francisco, Calif. 96239

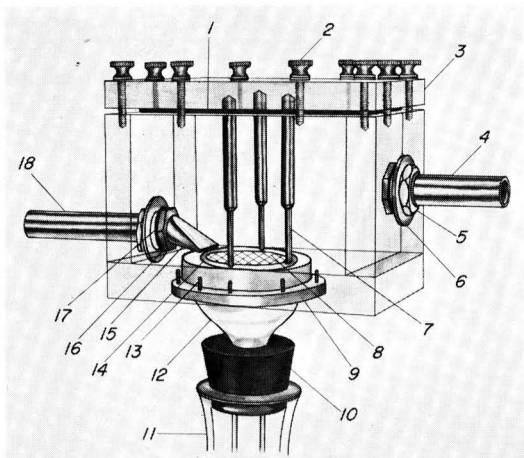


Figure 1. Continuous solids-liquid separation apparatus

(1) "O" ring seal for the removable top. (2) One of 10 screws to hold top on Plexiglas box. (3) Removable top. (4) Outlet port. (5) Nut to hold outlet port flush with side of apparatus. (6) Flange to distribute pressure from holding nut. (7) One of 3 spring-loaded shafts which hold filter in place. (8) Millipore filter, type HA (0.45 micron, 47 mm.). (9) Fitting to keep Millipore filter holder attached to the Plexiglas box. (10) Rubber stopper. (11) Vacuum suction flask. (12) Millipore filter holder. (13) Screws to attach fitting to Plexiglas box. (14) Stainless steel ring to distribute pressure from the 3 spring-loaded shafts to the filter paper. (15) Flow nozzle. (16) Nut to hold inlet port flask with side of apparatus. (17) "O" ring. (18) Entrance port

position by a circular stainless steel ring, which distributes the pressure from three spring-loaded shafts connected to the top of the box, and by the vacuum from below in the vacuum suction flask. The top is held in place by 10 screws and an "O" ring for an airtight fit. The top is removable for easy cleaning and filter service.

The separation device is shown schematically in Figure 2. The apparatus is placed on a vacuum suction flask and the pressure is lowered to 5 mm. of Hg or less. This seats the filter properly and supplies the driving force for the vacuum filtration. The solution to be filtered is then pumped from its reservoir (the activated sludge tank in this study) through the entrance port at a rate of 4 liters per minute. This circulation flow through the entrance nozzle is what causes the continuous washing effect on the filter. The thickened solution leaves through the exit port and returns to the activated sludge tank.

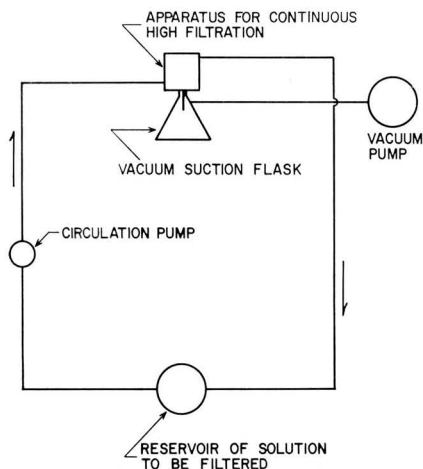


Figure 2. Arrangement used for separation process

Table I. Comparison of New Apparatus with Conventional Millipore

Time, Min.	Volume of effluent recovered at end time period, ml.	
	Conventional "batch" Millipore	New continuous Millipore
0	0	0
0.5	0.9	0.7
1.0	1.8	1.5
2.0	3.4	3.1
4.0	3.6	6.2
8.0	4.4	11.6
16.0	5.2	24.9
32.0	5.4	52.0
64.0	5.5	103.0

After dilution with the culture and appropriate residence time, determined by the culture's volume, it will again make another pass through the apparatus to be further thickened.

### Discussion

When the apparatus was connected to the activated sludge unit under study, an effluent was obtained which contained no particles having a diameter greater than 0.45 micron in accordance with residue determinations by the American Public Health Association (1965). Filtration rates were between 100 and 150 ml. per hour (depending on the viscosity of the solution and the age of the filter) with a pressure of 5 mm. of Hg or less in the suction flask and a circulation rate of 4 liters per minute of fluid through the nozzle. Table I compares the apparatus described with the conventional batch Millipore filter in terms of volumes of effluent recovered from our activated sludge unit per unit of time. This table is presented only to show how the conventional filter clogs after a few minutes while the nozzle apparatus extends the useful filtering life. The type HA (0.45-micron, 47-mm.) Millipore filter could be used to filter as much as 5 liters of effluent through the apparatus before it had to be changed, not because of clogging but because the filter paper started to wear as a result of the continuous high-speed flow of the fluid across its surface. Continuity of removal was maintained by having two units in parallel and switching total flow alternately through them as effluent accumulation or filter wearing required.

### Applications

The most obvious application for the apparatus is its use in bacteriologic and microbiologic research and pilot-plant studies for removing spent media from cultures on a continuous basis with high filtration efficiency. Many other potential applications also exist in chemical processing studies for clarifying liquids or dewatering solids. The units can be considered "modular" and numerous units can be connected in parallel if larger volumes per unit of time are required.

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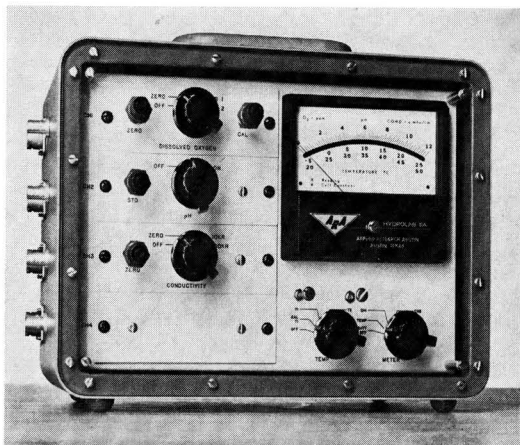
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**Air Pollution Monitoring Instrumentation—A Survey.** NASA AP-5072. vi + 74 pages. U.S. Government Printing Office, Washington, D.C. 20402. 40 cents, paper.

As part of the National Aeronautics and Space Administration's (NASA) technology utilization program, this survey serves to transfer air pollution monitoring technology, originally developed in aerospace research, to the general industrial domain. Thirty-two instruments and techniques are described in the survey, including gas and vapor control methods, particulate collection and monitoring systems, a gaseous hydrocarbon monitor, automatic aerosol particle counter, and air pollution monitors such as an ultraviolet densitometer and infrared tunable laser. ■

**Chemical Analysis of Industrial Water.** James W. McCoy. 350 pages. Chemical Publishing Co., Inc., 200 Park Ave. South, New York, N.Y. 10003. 1969. \$15.00, hard cover.

Aimed at chemical engineers and analytical chemists, the publication discusses and attempts to find solutions to such problems as water treatment, plant corrosion, and chemical analysis involved in chemical process industries, steam and power plants, and petroleum refining. ■

**Engineering Study of Removal of Sulfur Oxides from Stack Gases.** Richard Dennis and Ralph H. Bernstein. GCA-TR-68-15-G. v + 69 pages. American Petroleum Institute, 1271 Avenue of the Americas, New York, N.Y. 10026. 1968. \$1.50, paper.

Four major processes for the removal of sulfur oxides from flue gases were studied and evaluated, both economically and technically. The processes—dry dolomite injection-wet scrubbing, catalytic oxidation, alkalized alumina, and reinluft—were ranked on technical feasibility, state of development, process applicability, relative advantages, problems areas, and economic considerations. ■

**1967 Domestic Refinery Effluent Profile.** iii + 63 pages. American Petroleum Institute, 1271 Avenue of the Americas, New York, N.Y. 10020. 1968. \$3.00, binder.

The survey is a result of answers to a questionnaire distributed to the refining industry by API Committee on Air and Water Conservation. Responses—representing 93% of the industry's crude processing capacity—provided information on the waste water treatment and control practices, as well as final effluent quality at domestic crude refinery installations. ■

**Water, Health, and Society—Selected Papers by Abel Wolman.** Edited by Gilbert F. White. xii + 400 pages. Indiana University Press, Tenth and Morton St., Bloomington, Ind. 47401. 1969. \$15.00, hard cover. ■

**Measurement of Air Pollutants—Guide to the Selection of Methods.** M. Katz. 123 pages. World Health Organization, c/o American Public Health Assoc., 1740 Bdwy., New York, N.Y. 10019. 1969. \$5.00, hard cover. ■

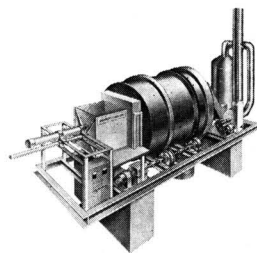
**Paints and Protective Coatings for Wastewater Treatment Facilities.** Manual of Practice 17. 88 pages. Water Pollution Control Federation, 3900 Wisconsin Ave., Washington, D.C. 20016. 1969. \$2.50, members, \$3.50, others; paper. ■

**Organochlorine Pesticides in the Environment.** Lucille F. Stickel. U.S. Department of the Interior SSRW-119. 32 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1969. 40 cents, paper. ■

**Waterfowl Status Report, 1968.** Edited by R. Kahler Martinson, James F. Voelzer, and Mildred R. Hudgins. U.S. Department of the Interior SSRW-122. 158 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1969. \$1.25, paper. ■

**Capital and Operating Costs of Sewage Treatment.** R.M. Bradley and Peter C. G. Isaac. Bulletin 40, University of Newcastle upon Tyne, Department of Civil Engineering. vi + 67 pages. Oriel Press, Ltd., 27 Ridley Pl., Newcastle upon Tyne, 1, England. 1969. \$2.50, paper. ■

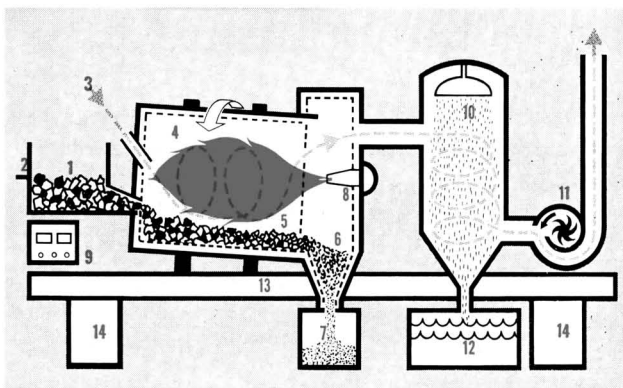
**The Subversive Science—Essays Toward an Ecology of Man.** Edited by Paul Shepherd and Daniel McKinley. 453 pages. Houghton Mifflin Co., 53 W. 43rd St., New York, N.Y. 10036. 1969. \$5.95, paper. ■



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The Series 1000 Carbon Monoxide Detection System is designed for hard service environments such as those in steel mills, sublevel parking garages, tunnels, and industrial plants. The units operate continuously, detecting CO in air in the 0-500 p.p.m. range, the company says. Alarm actuation is factory pre-set at 50 p.p.m.; units feature dust-tight splashproof construction; and a simple pump which furnishes continuous capacity will draw sample up to 500 feet distant without heat rise, and requires no lubrication. Designed to continuously monitor any sample area, and signal the presence of combustible gas or vapor in concentrations below the lower explosive limit, the Series 5000 Gas/Vapor Detection System have application in sewage treatment, pipeline storage stations, chemical process plants, and the like. Most models are available for rack, wall, or panel mounting, or table top use. Devco Engineering, Inc. 64

## Water treatment

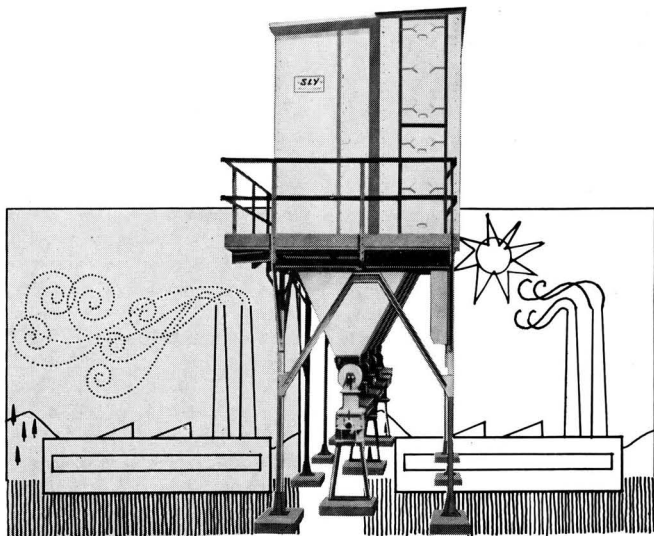
Skail-Away is a water treatment compound, odorless and nonfuming, which dissolves calcium and magnesium scale in water handling equipment. Featuring built-in color indicator to permit easy visual determination of the strength of the solution, the scale remover is available in liquid or powder form, and is effective at all temperatures, according to the company. Vulcan Laboratories, Inc. 65



## BOD bottle

The ConTech BOD Bottle, made of clear flint glass, with 250 ml. capacity, is available for use in the basic waste water analyses of biological oxygen demand (BOD). The company says the bottle features volumetric accuracy of  $\pm 1\%$ , allowing dilutions to be made directly in the bottle; liquid seal; large permanent etched marking area; and compact size. Consolidated Technology, Inc. 66

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**Clean air.** The Series 312 Dust Collector—described by the company as a high velocity centrifugal collector especially designed for limited space requirements—is discussed in Catalog F-1101. Applications, specifications, principle of operation, size and design factors, and recommendations for extreme operating conditions are included. Catalog F-1201 details the Series 322 Dust Collector, which is designed for efficient particle collection in the lower micron range. In addition to specifications, principle of operation, and performance record in various applications, the catalog includes a chart to guide in selecting a particular model of the 322 series. American Standard, Inc. **91**

**Auger spectroscopy.** The history and operation of Auger spectroscopy, and its applications in the study of surface composition and the nature of contaminants, surface segregation, surface dif-

fusion, and surface reactions are included in a 12-page brochure describing the Auger Electron Spectrometer. Specifications and drawings of the chief components of the instrument—which features 0.5% resolution for element identification—are included. Varian **92**

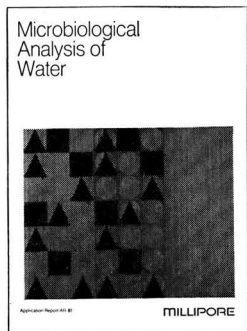
**Industrial waste.** A 20-page brochure describes the company's capabilities in the design, construction, and operation of industrial waste disposal and water supply systems. Photographs of installations and schematic drawings illustrate discussions of the various techniques and approaches used by the company in dealing with particular pollution problems. International Pollution Control, Inc. **93**

**Water pollution abatement.** A 6-page full color catalog describes the company's services in the design and engineering of packaged sewage treatment

systems, and lists its products. "Water Pollution Control Systems" discusses two types of systems—one based on extended aeration principles; the other on contact stabilization engineering—including schematic drawing, description, method of operation, and specific advantages. Lyco Systems, Inc. **94**

**Water analysis and monitoring equipment.** The company's line of instruments and equipment for analysis, monitoring, and control of water, wastes, and process liquids are listed in Bulletin 6. Summary information is given about such devices as the Model 310 Automatic Analyzers, Series 260 Photometric Analyzers, Model 1112 pH Meter, and Series 3000 Portable Self-Powered Analyzer/Recorders. The 8-page bulletin also includes prices and a selection table which indicates which equipment is used to perform different tests. Delta Scientific Corp. **95**

## We rewrote the book-



Describes improved procedures for the detection of fecal coliform, a new rapid screening method for algae, more complete data on total coliform analysis and a new section on pathogens, in addition to a detailed description of the Millipore method (an APHA standard) for the analysis of water and waste water. Millipore Corporation, Bedford, Mass. 01730.

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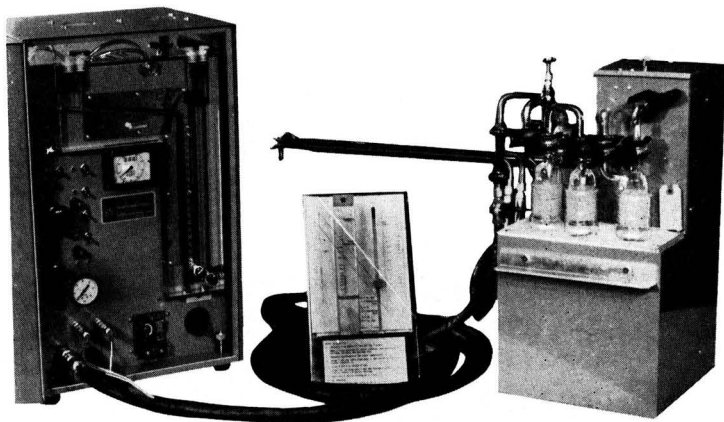
**Water treatment systems.** One company's adaptation of the Pintsch Bamag process for the removal of scale and free rolling oils from waste water in hot rolling mills, continuous casting systems, and similar facilities is described in Bulletin No. 68WWT07. Design, construction, and operation of its mill scale water treatment system—which the company says requires 50% or less of the area necessary for similar types of installations—are covered in the publication. Dravo Corp. 96

**Packaging and solid waste.** A 200-page report (PHS Publication 1855), "The Role of Packaging in Solid Waste Management 1966-76" is the result of a two year study conducted by Midwest Research Institute under the auspices of HEW's Environmental Control Administration. Purpose of the study was to define the role of packaging materials, such as paper, metal, glass, wood, plastics, and textiles, in refuse disposal problems for the ten year period (ES&T, April 1969, page 328). Environmental Control Administration, U.S. Dept. of Health, Education, and Welfare, 222 E. Central Pkwy., Cincinnati, Ohio 45202. (Write direct)

**Solid waste.** Public Health Service Publication No. 1748 details a special incinerator study for the District of Columbia. The study discusses optimal incinerator plant design which can be used for solid wastes management in other communities. Estimates are presented for capital and operating costs of air pollution equipment for particulate emissions control. Environmental Control Administration, Federal Solid Wastes Program, 222 E. Central Pkwy., Cincinnati, Ohio 45202. (Write direct)

**Solid waste.** "Collection and Disposal of Solid Waste for the Des Moines Metropolitan Area" is an interim report on a systems engineering approach to the problems of solid waste management for a population of 288,000 in an area of 430 sq. mi., including 12 cities and towns and two counties. The 326-page report was prepared by the engineering firms of Henningson, Durham, and Richardson (Omaha, Neb.) and Veenstra and Kimm (Des Moines, Iowa). Bureau of Solid Waste Management, 222 E. Central Pkwy., Cincinnati, Ohio 45202. Refer to Demonstration Project D01-UI-00060. (Write direct)

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**July 14-16**  
**American Society of Civil Engineers,**  
**Sanitary Engineering Division**

2nd National Symposium on Sanitary Engineering Research, Development, and Design

Cornell University, Ithaca, N.Y.

More than 30 papers will be presented at the 10 technical sessions of this year's meeting. Topics to be covered include analysis and design of water resource systems, activated sludge design and new concepts in solids handling, waste water treatment processes, and solid wastes.

**July 22-25**  
**University of Rhode Island**

Annual Northeast Regional Anti-Pollution Conference (ANERAC II)

University of Rhode Island, Kingston

The technical program will include sessions devoted to discussion of marine pollution, waste water, air pollution, and solid waste disposal. For further information, contact: C. J. Wilson, Bliss Hall, University of Rhode Island, Kingston, R.I. 02881

**July 28-August 1**  
**Instrument Society of America**

Research Conference on Instrumentation Science

Hobart and William Smith College, Geneva, N.Y.

Designed to provide informal discussion of new developments in major areas of instrumentation science research, the conference will feature state of the art presentations and problem solving sessions, as well as discussion of new work in the field. Topics for discussion include instruments and the environment, instruments in extreme environments, and pollution monitoring and control.

**August 4-8**  
**Engineering Foundation**

Research Conference on Particulate Matters Systems

Deerfield Academy, Deerfield, Mass.

Designed to bring together people interested in all aspects of particulate science, the conference will feature discussion of such topics as pipelining of solids, particle size measurement, and surface chemistry applied to dispersion, agglomeration, and flotation. Attendance limited. For information: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

**August 4-8**  
**Engineering Foundation**

Research Conference on Technology Assessment

Proctor Academy, Andover, N.H.

The sponsors define technology assessment as the process of identifying and studying the special, economic, and environmental consequences of the application of science. Such problems as automotive air pollution, sonic boom, and oil spills from offshore installations fall within this category. The conference will feature reports and discussion in an informal atmosphere for the purpose of defining the state of the art, proposing studies, and soliciting new approaches to methodology. Enrollment limited.

**August 18-22**  
**Engineering Foundation**

Research Conference on Water Pollution

University of California, Santa Barbara

National Goals in Water Pollution Control is the theme of this year's meeting. More than 100 leaders in engineering and related disciplines will discuss the deficiencies in national policies, especially in the areas of beneficial water uses, establishment of water quality standards, financial incentives, government support for facilities, and public involvement in the problem.

**Courses**

**July 14-23**  
**Massachusetts Institute of Technology**

Summer Program in Semipermeable Membranes

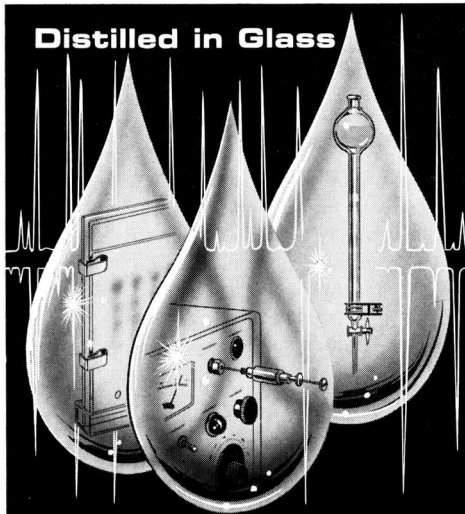
M.I.T., Cambridge, Mass.

Designed for chemical engineers, industrial chemists, and others interested in separation by membranes, the course will cover classical and novel semipermeable membranes. Applications of membranes into larger total systems, such as protein dialysis and water desalination, will be included.

**August 11-23**  
**University of Wyoming**  
**College of Law**

Short Course in Water Resources Law  
Land and Water Law Center, Laramie, Wyo.

The two-week course is aimed at non-lawyers, including scientists, engineers, economists, administrators, and graduate students in water resources management. Some of the topics to be covered are riparian rights, pollution control, groundwater law, and public rights to waters. Two hours credit will be given. For information: Michael V. McIntyre, P.O. Box 3035, University Station, Laramie, Wyo. 82070



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## meeting guide

### September 22-26 University of California

Short Course on Combustion-Generated Air Pollution

University of California, Berkeley

The 5-day intensive course is planned to cover fundamental knowledge and current practice, and will include lectures and discussion on such topics as combustion and combustion kinetics, environmental effects of air pollution, control techniques, and emissions sources. For information: Continuing Education in Engineering, University Extension, 2223 Fulton St., Berkeley, Calif. 94720

### Special Notices

#### 1969-1970 Academic Year Cornell University

Graduate Programs in Agricultural Waste Management

Opportunities for graduate study and research are offered in an extensive multidisciplinary program in agricultural waste management. Areas of study include water resources engineering, agronomy, and animal science; research activities include liquid waste treatment, land disposal, and odor reduction and control. Research assistantships, associatehips, and other financial support are available. For details write: Field Representative, Department of Agricultural Engineering, Riley-Robb Hall, Cornell University, Ithaca, N.Y. 14850

#### 1969-1970 Academic Year University of Colorado, Boulder

Federal Water Pollution Control Traineeships

Financial assistance is available for graduate study in water resources and sanitary engineering. Applicants with a background in engineering or science will be considered for the grants. Annual stipends for master's candidates are \$2400 per year plus \$500 per dependent. Those interested in graduate programs in water resources engineering or chemical and microbiological aspects of water resources should contact: Director, Water Resources Program, Engineering Center OT 4-34, University of Colorado, Boulder, Colo. 80302

#### 1969-1970 Academic Year University of Florida Department of Environmental Engineering

Environmental Research Program in Terrestrial Ecology

Applications will be accepted for admission to a program of environmental research in tropical and subtropical terrestrial ecosystems. Emphasis of the project-oriented program is on the team approach, combining such specialists as agronomists, ecologists, entomologists, and the like, with environmental engineers, health physicists, and radiochemists. Research topics are available at the masters, doctoral, and postdoctoral level. Contact: Terrestrial Ecology Research Program, Department of Environmental Engineering, University of Florida, Gainesville, Fla. 32601

(Continued on page 685)

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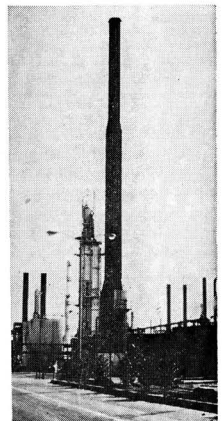
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**1969-1970 Academic Year  
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as for postdoctoral studies. Recipients participate in multidisciplinary programs designed to prepare students for careers in research, teaching, and practice in the various specialized fields in environmental health. For details: Institute of Environmental Health Studies, Box 630, Chapel Hill, N.C. 27514

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International Association on Water  
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5th International Conference on Water Pollution Research  
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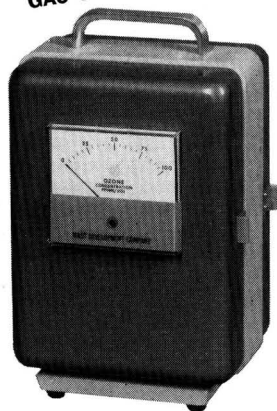
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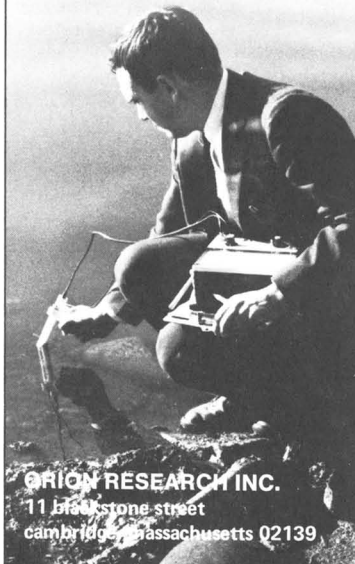
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