

ENVIRONMENTAL Science & Technology

Emphasizing

Water,

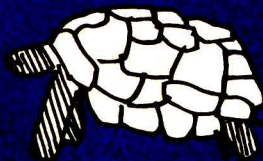
Air, &

Waste

Chemistry

OCTOBER 1967

Preserving a living labora-
tory 778



Water management, a
fashionable topic 780

Equipment market for
water pollution control
785

Developing an overall air
pollution index 796

Cadle reviews *The Particle
Atlas* in fact, theory, and
practice 849



Dramatizing a regional air
pollution problem 792

Current Research 801

**TOXIC
WASTE
DISPOSAL?**

**POLLUTION
CONTROL?**

**NALCO
ION EXCHANGE EXPERTS
CAN HELP YOU
FIND ANSWERS!**

Nalco experience with ion exchange goes back to siliceous zeolites and green sand—includes patents on ion exchange resins and processes! Recent new Nalco ideas include Sul-bi-Sul[®], a low-cost, high-efficiency method of sweetening brackish waters; a self-regenerating ion exchange method to keep the hot end of multi-stage evaporators scale-free in a kind of “perpetual-motion” sequence; and some ingenious new ways to recover metals and control pollution for problem-plagued processors.

We can put this unmatched experience and creative problem-solving ability to work for you. We'll act as consultants to work with your staff, or develop answers through contract research—or both—all on a confidential basis. And, Nalco is geared to deliver practical answers, not fancy theories.

Write or call L. F. Wirth, Jr. of our Ion Exchange Division in Chicago (Phone: 312-767-7240). Let's see if Nalco can help you.

Send For Free Bulletin:

**“Ion Exchange
in Chemical
Processing”**

Basic technical data on ion exchange materials, and their potential uses in processing.



Nalco

NALCO CHEMICAL COMPANY
180 N. MICHIGAN AVENUE • CHICAGO, ILLINOIS 60601

Circle No. 6 on Readers' Service Card

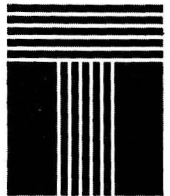
Now, a complete water quality program.

Measure 1, 2, or any 12 water pollutants... automatically, continuously and specifically.



COPYRIGHT © 1967 BY TECHNICON CORPORATION

You may want to quantitate COD, phenols, cyanide, ammonia nitrogen, or any one of a host of pollutants. You may even want to quantitate 12 at one time. Technicon® AutoAnalyzer® systems, employing Standard Methods, give you this flexibility, as well as accuracy and specificity. Around-the-clock watch on vital water quality measurements can be returned within 15 minutes. Low maintenance enables a network of these monitors to be established at extremely low cost. The Technicon brochure CSM-12 explains how the limitation of exactly measuring the many possible pollutants is removed by continuous on-site monitoring. Write for it. Dept. G, Technicon Corporation, Ardsley, New York 10502.



Circle No. 15 on Readers' Service Card

ENVIRONMENTAL Science & Technology

Volume 1, Number 10
October 1967

Editor: James J. Morgan
Managing Editor:
Melvin J. Josephs
Assistant Editor:
Stanton S. Miller
Editorial Assistant:
Nancy M. Campbell
Manager, Manuscript Reviewing:
Katherine I. Biggs
Manager, Manuscript Editing:
Ruth Reynard
Director of Design:
Joseph Jacobs
Production Manager:
Bacil Gulley
Layout and Production:
Norman W. Favin
Production—Easton, Pa.
Associate Editor:
Charlotte C. Sayre
Assistant Editor:
Elizabeth R. Rufe
Advisory Board: A. P. Altshuler, W. L. Faith, S. K. Friedlander, A. F. Gaudy, Jr., E. D. Goldberg, H. P. Gregor, T. E. Larson, G. F. Lee, J. N. Pitts, Jr., W. Stumm

American Chemical Society Publications
1155 Sixteenth St., N.W.
Washington, D. C. 20036

Director of Publications:
Richard L. Kenyon

Director of Business Operations:
Joseph H. Kuney

Publication Manager, Journals:
David E. Gushee

Executive Assistant to the Director of Publications: Rodney N. Hader

Circulation Development Manager:
Herbert C. Spencer

Assistant to the Director of Publications:
William Q. Hull

Advertising Management:
Reinhold Publishing Corporation
For list of offices, see page 864
For list of advertisers, see page 864

© Copyright 1967, by the American Chemical Society

SUBSCRIPTION SERVICE: All communications related to handling of subscriptions, including notifications of CHANGE OF ADDRESS, should be sent to Subscription Service Department, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Change of address notification should include both old and new addresses, with ZIP numbers, and be accompanied by mailing label from a recent issue. Allow four weeks for change to become effective.

SUBSCRIPTION RATES 1967: Members, domestic and foreign, 1 year \$5.00; nonmembers, domestic and foreign, \$7.00. Postage: Canada and Pan-American Union, \$1.00; all other countries, \$1.50. Single copies: current issues, \$1.00. Postage: Canada and Pan-American Union, \$0.15; foreign, \$0.20. Rates for back issues or volumes are available from Special Issues Sales Dept., 1155 Sixteenth St., N.W., Washington, D. C. 20036. Claims for missing numbers will not be allowed if received more than 60 days from date of mailing plus time normally required for postal delivery of journal and claim. No claims allowed because of failure to notify the Subscription Service Department of a change of address, or because copy is "missing from files."

Published monthly by the American Chemical Society, from 20th and Northampton Sts., Easton, Pa. 18042. Executive Offices, Editorial Headquarters, and Subscription Service Department, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Advertising Office: 430 Park Ave., New York, N. Y. 10022. Second class postage paid at Easton, Pa. 18042.

The American Chemical Society assumes no responsibility for the statements and opinions advanced by contributors to its publications.

Please send manuscripts to:
Manager, Manuscript Reviewing
1155 Sixteenth St., N.W.
Washington, D. C. 20036

ESTHAG

Editorial

Countdown for positive pollution control is well under way as a restless public seeks some action 771

Environmental Currents

Male twins are sought for environmental research 773

Gasbuggy's A-blast may yield sulfur-free natural gas 773

Call for leaded gasoline standards may start a row 773

Move made for Department of Natural Resources 774

Seedings of hurricanes must await new trials 774

CIRES aims at environmental science research and teaching 775

Laboratory ships help FWPCA control pollution 775

Coal-fired power plant installs dolomite system 775

Computers control input to storm and sanitary sewers 777

Congress may propose Council of Ecological Advisers 777

Outlook

Aldabra's unique ecosystem is threatened by defense plans, but scientists are rushing to its rescue 778

Water management of the Earth's relatively constant supply is both fashionable and necessary 780

Water pollution control equipment market may reach tens of billion dollars in next several decades 785

Radio station programs Philadelphia's air pollution problems for one full day's discussions 792

Feature

Air Pollution studies can be aided by an overall air pollution index carefully developed and used 796

Bookshelf

Particle identity in fact, theory, and practice. A review by Richard D. Cadle of "The Particle Atlas" 849

Latest analyses for pesticide residues. A review by Howard A. Jones of "Residue Reviews. Vol. 17: Residues of Pesticides and Other Foreign Chemicals in Foods and Feeds" 850

Exchange of ideas on fresh water. A review by William C. Ackermann of "The Fresh Water of New York State: Its Conservation and Use," a symposium 852

New Products Digest 854

New Literature Digest 859

Meeting Guide 861

Professional Consulting Services Directory 863

CONTENTS

Current Research

Response of single particle optical counters to nonideal particles 801

K. T. Whitby and R. A. Vomela

Three single particle counters differ in their response to nonideal but monodisperse aerosols. The Royco PC 200 and the Southern Research Institute counters, which accept light through only a small solid angle, indicate a considerable spread in size distribution for aerosols of India ink and polystyrene. The Bausch and Lomb counter, which accepts light through a much larger solid angle, gives better resolution.

The proximate calculation of the solubility of gypsum in natural brines from 28° to 70° C. 815

A. V. Metler and A. G. Ostroff

The solubility of calcium sulfate in natural brines can be calculated by a method which recognizes the interdependence and influence of salinity, kind of salinity, and temperature. The method overrides inadequacies of the Debye-Hückel theory for the more concentrated solutions. Specifically designed for use by engineers involved with handling of field brines, the method requires a minimum number of calculations and conversions.

Biodegradation of nitrilotriacetate in activated sludge 820

R. D. Swisher, M. M. Crutchfield, and D. W. Caldwell

If nitrilotriacetate becomes an important component in detergent formulations and so finds its way into domestic sewage, it should have no significant effects on the general environment. The activated sludge sewage treatment process readily degrades NTA, as evidenced by loss of its chelating properties. The most likely intermediate degradation products would be glycine and glycolic acid. Since they are natural metabolic intermediates in living cells, they should enter the natural biochemical processes with no difficulty.

Gas chromatographic analysis of polycyclic aromatic hydrocarbons in soot samples 828

B. B. Chakraborty and Ronald Long

Carcinogenic compounds found in urban soot samples can be identified and determined by a relatively rapid method using programmed temperature gas chromatography and dual flame-ionization detectors. Analyses of simulated soots from ethylene and ethane diffusion flames identified 15 polycyclic aromatic hydrocarbons. Most of the major components have already been shown to be present in diesel and automobile exhaust products and in air particulates, but five of the hydrocarbons were identified apparently for the first time. These include methylphenanthrenes, benzo[ghi]fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-cd]pyrene.

Catalytic combustion of ethylene on nickel oxide 835

A. E. Cohen and Ken Nobe

Nickel oxide catalysts can oxidize hydrocarbons completely to CO₂ and H₂O at reasonably low temperatures. Research workers used initial concentrations of 500 to 1200 p.p.m. of ethylene, to approximate concentrations in the exhausts of various combustion devices used in auto engines and power plants. Combustion was studied in the temperature range of 260° to 370°C. Below 350° C., pore diffusion had only a negligible effect on the combustion kinetics of nickel oxide catalysts. Comparing the combustion characteristics of nickel oxide catalysts with those of copper oxide, the research workers conclude that nickel catalysts are not as effective as copper catalysts.

Communications

Occurrence of beryllium as a trace element in environmental materials 839

W. R. Meehan and L. E. Smythe

Foodstuffs, human organs, plants, soil and water, and marine life from an Australian environment contain trace amounts of beryllium. In almost all cases, concentrations are below 1 p.p.m. The morin method, which has a practical limit of 2×10^{-5} µg Be/ml., was used. Values for foodstuffs generally range from 0.01 to 0.1 p.p.m., with oyster flesh and mushrooms having the highest values. The highest value for human organs is for lungs. There was little evidence for any beryllium concentration mechanism in plants.

Photooxidation of formaldehyde at low partial pressures of aldehyde 845

T. C. Purcell and I. R. Cohen

Hydrogen peroxide is produced by the photooxidation of formaldehyde at low partial pressures of aldehyde. Formaldehyde at concentrations ranging from 1 to 30 p.p.m. in air was irradiated in reaction containers fabricated from fluorinated ethylene-propylene copolymer. The apparent molecular imbalance between peroxide formed and formaldehyde consumed is attributable, at least in part, to surface effects related to the reaction container.



**The White House is talking about it.
Congress is talking about it.
Your boss is talking about it.
Your wife is talking about it.**

Talk to us. Because we've developed a system that can handle large and extremely complex wastewaters economically—SURFPAC® biological oxidation media.

SURFPAC media provides the most efficient environment for microorganisms to aerobically degrade waste materials. Its two-way corrugation exposes maximum surface area to biological activity (more than twice the area of three-inch rock). And it has more than double the normal void space of conventional rock or slag trickling filter systems. Naturally, increased capacity is possible. State-approved organic loadings, based on successful performance of full-scale units, are four times greater than those for rock for the same treatment level. Likewise, the minimum hydraulic loading for SURFPAC is greater than the maximum suggested for rock trickling filters.

Sedalia, Missouri, is a good place to see how well SURFPAC really works. Two parallel filters receive wastewater at a rate of 32 mgad. Waste entering the filters has a BOD of 345 mg/1. Removal in the secondary process alone is 90%. The towers occupy only a fraction of the space normally required by conventional rock trickling filters.

Each is 75' in diameter with a media depth of 12.6'. Eight 6'-deep rock filters, having the same 75' diameter, would have been necessary for the same treatment. That's a 75% reduction in land area alone. And the city enjoys a substantially lower overall cost.

SURFPAC media was the answer for Sedalia and other cities and industries faced with increased waste treatment requirements. It's probably the answer for you, too. It's worth talking about. The Dow Chemical Company, Midland, Michigan 48640.



Circle No. 2 on Readers' Service Card

Countdown for positive pollution control is well under way

Current public restlessness to do a vague something about pollution control is rapidly consolidating into an action type program

If one can cut through the fog of flippancy, he can find much of value in a well-planned 18-hours-long radio program devoted almost entirely to the subject of air pollution. Just such a program was produced this month by station WCAU in Philadelphia. It is covered, mostly in pictorial form, in this issue (page 792).

An ES&T reporter-editor spent the full day in the station's studios. He noted that the discussions, which involved station talk masters, interested citizens, informed professionals, expert observers, and knowledgeable politicians and public servants, were often superficial and diffuse, but, now and then, factual and pointed.

The discussions stimulated a variety of comments from some of the almost three quarters of a million listeners tuned in that day. The following comments are typical of those made by both listeners and discussants during the day's events:

- The problems of air pollution are insidious. We may conclude that where physiology is affected, psychology is also affected.
- The pollution situation will worsen for the next few years, and all major cities are sitting on a pollution powder keg. A disaster could easily come from the interaction of an inversion and a day of heavy air pollution.
- Industry plans to spend \$73 million for pollution control, whereas car owners are being prepared to spend \$400 million.
- Air pollution control is no longer strictly a technical matter. Now it is an economic and social (health) problem as well.
- Industry is trying to meet the minimum levels of the law, but is not really fired up to solve the problems.

• Fines are not the way to achieve pollution control. Abatement will be accomplished only by putting the deliberate offender out of action.

• Names of offenders should be published so consumers can boycott the guilty.

• Even though much air pollution may be caused by individuals, the fact is that individuals have very little to say about what is done to correct it. Thus, more control by government officials is needed.

• The main reason for the current movement of pollution control bills is the tremendous groundswell of public opinion.

What all these comments mean, really, is that the public is fully aware of the need to do something—albeit a vague something—about pollution. The public is eager to ameliorate a difficult situation. It is convinced of the danger. And it is convinced of its inability, as individuals, to do anything meaningful.

Citizens know, too, that no matter who pays for what, they, as consumers and taxpayers, will end up with the real bill. And overall they seem resigned to accept that responsibility.

From the evidence, WCAU's full day of public service broadcasting did not fulfill its fond hopes that listeners now would be fully convinced that air pollution is a major menace to today's society. But in the degree that it failed, it failed only because the listeners already knew of the menace, at least in part. And they clearly demonstrated a restlessness to solve the matter quickly, efficiently, and permanently.

The restlessness is building. Those in industry and government taking appropriate control actions may escape the gripes and the wrath of an aroused citizenry. Those doing little or nothing are in for a widely heralded, rapidly approaching, vexatious judgment day. The countdown is under way.

William J. Josephs

Detectability and system linearity identify the H-P Model 402 High-Efficiency Gas Chromatograph

A high-efficiency gas chromatograph is a complex instrument with a long list of specs that tend to obscure its real function, which is analytical performance. Reduced to this fundamental, the high-efficiency gc can be positively identified by two characteristics:

Detectability. Does it detect small quantities of hard-to-chromatograph substances? In other words, if you inject a nanogram, say, of an easily degradable material such as a steroid, will it analyze it without decomposition to produce a usable chromatogram? If it does, it has detectability, a system characteristic which is substantially more meaningful than the usual "detector sensitivity" found in a typical list of specs.

System Linearity. Does it respond proportionately to different amounts of hard-to-chromatograph substances? In other words, if you inject exactly twice the amount of that same material, will it produce a recorder peak size that's exactly twice as large? If it does, it has system linearity, a char-

acteristic that is incalculably more important than the usual "detector linearity" spec.

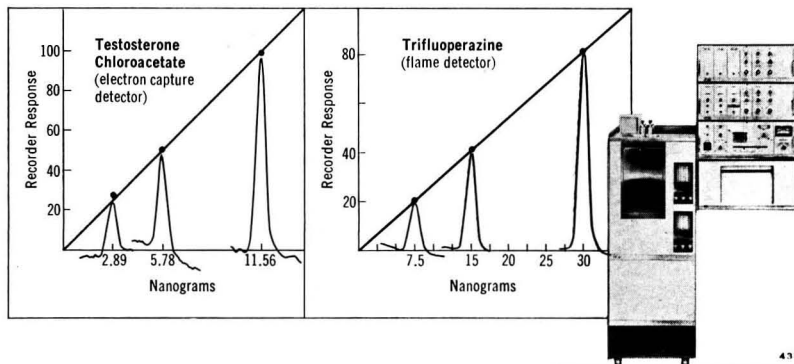
In the two series of chromatograms reproduced here, we offer convincing evidence that the H-P Model 402 High-Efficiency GC possesses system detectability and linearity to an almost perfect degree. In the first place, both trifluoperazine and testosterone chloroacetate are hard-to-chromatograph substances . . . and the 402 detected both in the nanogram range. Moreover, a quick glance at the linearity plot will show that the 402's response closely approaches the theoretical ideal.

You can get full information by writing for Bulletin 4020 (. . . it contains a "long list of specs") or by calling the nearest H-P sales office. Prices start at \$3700.00.

Hewlett-Packard, Route 41, Avondale, Pa. 19311. In Europe: 54 Route des Acacias, Geneva, Switzerland. Elsewhere: 1501 Page Mill Road, Palo Alto, California 94304.

HEWLETT  **PACKARD**
ANALYTICAL INSTRUMENTS

Superimposed on these two system linearity plots are the actual recorded peaks, accurately reproduced from the original chromatograms in the same scale.



Circle No. 4 on Readers' Service Card

Male Twins Sought for Environmental Research

Some 8000 pairs of male twins between the ages of 45 and 50 are being asked to participate in a study sponsored jointly by PHS and AMA.

The study seeks information on the relationship of such environmental factors as tobacco smoking and air pollution to certain cardiovascular and respiratory complaints. "In the present research, we shall find among the twins some pairs who have experienced different environmental exposure but are similar in all other respects," say scientists of the NAS and Drs. Lars Friberg and Rune Cederlof, visiting scientists from the National Institute of Public Health of Sweden. These pairs were selected from NRC's Twin Registry, a roster of male twins compiled during a 12-year period from the medical and vital statistics records of World War II veterans.

Gasbuggy May Yield New Source of Sulfur-free Fuel

In middle November, the AEC, in cooperation with the Bureau of Mines and the El Paso Natural Gas Co., will set off a subterranean atomic device (26-kiloton magnitude) to free natural gas held in the rock stratum in the Carson National Forest of northwestern New Mexico. Known as Project Gasbuggy, the joint venture will attempt to stimulate production and increase the ultimate recovery of natural gas. According to a Bureau of Mines' estimate, Gasbuggy may add as much as 300 trillion cubic feet of natural gas to the Nation's proved recoverable reserve—more than double the known reserve. Natural gas is sweet—essentially free of any sulfur compounds—and so may find immediate use in domestic heating, in preference to oil, thus helping cities in their fight for cleaner air.

Putting the Lid on Leaded Gasoline

"The Federal Government should immediately establish standards for the lead content in gasoline which will prevent any further increase in the total quantity of lead emitted to the atmosphere." This is one of the recommendations of "The Automobile and Air Pollution," a special report just submitted to the Commerce Department. "The major fears from rising lead levels in the environment stem from a belief that many of the adverse health effects may be chronic or cumulative and not early, or easily, detectable," according to the report. This recommendation will probably provoke controversy, considering the economics of converting to lead-free gasoline (ES&T, May, page 369). The report was prepared by the Panel on Electrically Powered Vehicles, MIT's Richard S. Morse, chairman. Early in its electric vehicle studies, the panel, realizing its scope was too limited, focused on the broader topic of auto and air pollution. The panel also calls for stepped up research efforts and tighter auto emission standards. As for electrically powered vehicles, they are at least a decade away from having "a significant impact in reducing the Nation's total air pollution," the panel concluded.

Department of Natural Resources

SECRETARY OF NATURAL RESOURCES

Deputy Secretary of Natural Resources

Under Secretary of Land Resources

Assistant Secretary for Land Resources Forest Service (from Agri.) Bureau of Land Management	Assistant Secretary for Recreation and Wildlife National Park Service Fish and Wildlife Service Bureau of Outdoor Recreation	Assistant Secretary for Minerals and Fuels Bureau of Mines Geological Survey Office of Coal Research	Assistant Secretary Air Pollution Abatement Program (from HEW) Solid Waste Program (from HEW)
--	---	---	---

Under Secretary of Water Resources

Bureau of Reclamation Civil works function Corps of Engineers (from Army) Soil Conservation Service (from Agri.) Water Pollution Control Authority Coordination of river basin plans with the Federal Power Commission Bonneville Power Administration Southwestern Power Administration All agencies in Interior having water resources matter as their principal concern.	Assistant Secretary for Oceanography Oceanographic Data Center (from Navy) Sea Grants Program (from NSF)
--	--

Proposal Advanced for Department of Natural Resources

Legislation to improve coordination of the activities of the many federal agencies having responsibilities in the natural resources field has been introduced. S. 886 would redesignate the Department of Interior as the Department of Natural Resources and transfer some agencies to and others from the new department. In commenting on the proposed legislation, Mr. Frank E. Moss (D.-Utah) stated that our needs in resource development and conservation have simply outrun our agency structure. Among other proposed changes the Bureau of Indian Affairs and the Office of Territories, now in Interior, would be moved to HEW.

No Seedings of '67 Hurricanes

From August 8 to October 15 scientists of the National Hurricane Research Laboratory of ESSA's Institute for Atmospheric Sciences participated in Project Stormfury. Basically, the objective of this continuing project is to learn whether a hurricane's violence can be lessened or altered by seeding the storm's clouds with silver iodide. By seeding clouds around the eye of the storm the latent heat of fusion of the droplets may be released and this release may trigger a chain of events leading to a redistribution of the storm's energy and a reduction in maximum wind velocities. Although the seeding area was modified from that of previous years, all the 1967 hurricanes failed in at least one way to qualify for the experiments. Seedings in previous years gave encouraging results, but conclusive evidence must await another year's trials.

ESSA + CU = CIRES

The Environmental Science Services Administration and the University of Colorado joined forces to form the Cooperative Institute for Research in Environmental Sciences (CIRES). The goal is to improve research, teaching, and training in environmental sciences. To be located in Boulder, CIRES is patterned after the Joint Institute for Laboratory Astrophysics, established in 1962 by the university and the National Bureau of Standards. Initially, CIRES will involve CU's departments of aerospace engineering sciences, astro-geophysics, chemistry, electrical engineering, geological sciences, mechanical engineering, physics, and astrophysics. Selected members of these departments and of ESSA will be in the institute, with visiting members coming to Boulder for stays of a year or so.

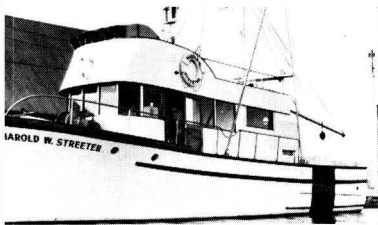
FWPCA Sends One Ship East, Another West

First of their kind in the field of water quality management, the *H. W. Streeter* and *Clean Waters* are floating laboratories equipped with the latest sampling and navigational devices to help with FWPCA's pollution control work. The recently commissioned *Clean Waters* is a 65-ft. vessel, and will operate in East Coast waters such as those of New York Harbor, the Hudson River, its tributaries, and offshore waters of FWPCA's northeast region. Commissioned in 1963, the *H. W. Streeter* is a 45-ft. vessel and will operate in West Coast waters. These vessels and their crews will perform a variety of functions, including:

- Surveillance in connection with the enforcement of federal standards.
- Evaluations of the effects of pollution on the estuaries and estuarine zones of the North Atlantic area.
- On-the-spot studies and provision of laboratory facilities in the event of oil pollution problems.
- Special oceanographic and biological studies relating to water pollution control.
- Data collection and laboratory analyses for comprehensive water pollution control programs.
- Training of personnel for water quality management.

Power Generating Plant Installs Dolomite System

This country's first full-scale demonstration of the dolomite system will be in operation early next year at Union Electric's coal-fired plant in Meramec, Mo. Developed by Combustion Engineering, Inc., the system removes at least 83% of SO₂, all SO₃, and more than 99% of the fly ash from stack gases. Earlier pilot plant and field tests indicated that the system might remove 98% of the SO₂, all SO₃, and 99% of the fly ash. The system involves the air injection of pulverized dolomite into the furnace where it is calcined to produce a more reactive compound. These calcined particles react with the SO₃ in the flue gas, thus preventing low temperature corrosion. The next step is wet scrubbing to dissolve calcium and magnesium oxides, and to permit the reaction of SO₃ with these dissolved oxides to form sulfates and sulfites of calcium and magnesium. The wet scrubbing also eliminates the fly ash.



Somewhere in your plant you've probably got a water problem.

A Calgon Water Audit™ can help you solve it at realistic cost.

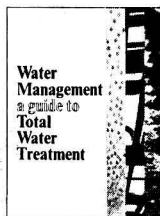
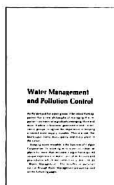
One of the most urgent problems facing industry today is the proper management of water. From the time water enters a plant until it leaves as waste water, more and more care must be taken to be sure that the water is treated and used properly.

Two informative booklets: "Water Management—A Guide to Total Water Treatment" and "Water Management and Pollution Control" outline a practical approach to water problems. They explain the benefits of a fact-gathering study of water use in industrial plants and outline the essential steps in a pollution control program. These procedures are being successfully followed today in many industrial plants throughout the country.

For information that will help clear up the confusion on the subject of water pollution, please fill out and mail the coupon.

Mr. W. H. Weitzel, Vice President
Calgon Corporation, Dept. W
Calgon Center, P. O. Box 1346
Pittsburgh, Pa. 15230

Please send me a complimentary copy
of "Water Management—a Guide to
Total Water Treatment" and "Water
Management and Pollution Control."



Name _____
Title _____
Company _____
Street or Box No. _____
City _____ State _____ Zip _____

Helping America answer the challenging problems of water



Circle No. 35 on Readers' Service Card

Computers to Control Combined Sewers

The Minneapolis-Saint Paul Sanitary District estimates it would take \$200 million and many years to separate its storm and sanitary sewers. Instead, the district is working on a \$1.7 million demonstration project to use a process control computer to get the most out of its present combined sewers. When heavy rainfall causes the sewers to overflow, the excess is diverted into the river through gates in the sewers. The job of the computer will be to see that the most polluted flow goes to the treatment plant and the cleaner water to the river. The system will rely on data telemetered from 28 sampling stations to the computer at the plant. The data will include the amount of rainfall, sewer levels, and gate positions; five stations will continuously telemeter six chemical and physical measurements on water quality. Using simulation techniques, sewage plant operators can determine the best settings on control gates to get maximum use of the plant and minimum pollution of the river. Key contract in the project, which is scheduled for completion in the spring of 1968, goes to Badger Meter Manufacturing Co. Under a \$387,105 contract, the company will install the computer and the remote telemetering and supervisory control equipment at the stations. To help support the project, FWPCA awarded a matching fund demonstration grant in June 1966. Detroit and Seattle later received grants for similar projects.

Council of Ecological Advisers Proposed

"Our environment is our most immediate need; it affects us every minute of the day, and the ecology of that environment can alter our lives," said Mr. John V. Tunney (D.-Calif.) on the occasion of introducing H.R. 13211. To be cited as the Ecological Advisers Act of 1967, H.R. 13211 provides for the creation of a council of ecological advisers in the Executive Office of the President. The council will take a comprehensive look at the ecology of our environment—from the point of view of man and his needs and the council will not occupy itself with the narrow definition of each constituent element of the environment. In proposing this bill, Mr. Tunney stated that there is a need to see that those areas of the government dealing with various environmental problems are able to bring all resources to bear on those problems, are using all of the material available to the Federal Government, are not duplicating other efforts and are far reaching and creative in their efforts—with an understanding of the relationship of their projects and work to other places in the public and private realms. Representatives of science, industry, and areas that are major concerns of environmental quality should be included in this council. Mr. Tunney feels that the larger part of the council's membership should be composed of social scientists, social and community planners, and public administrators. These advisers should be capable of supervising the overall program without becoming involved with the particulars of the various programs which come under the purview of the council.

Aldabra's unique ecosystem is threatened by British Government plans to develop the island for defense purposes, but the world scientific community is rallying to . . .

Preserve A Living Laboratory



Last stand. *The Old World species of giant land tortoise once inhabited most of the islands of the southwest Indian Ocean. Today it is found only here on Aldabra Island. Its closest living relative is the famous tortoise of Galapagos Islands, on the other side of the world from Aldabra*

Zoological curiosity shop, living natural history museum, biological treasure house, living laboratory—all have been used to describe Aldabra Island, a 60-square-mile coral atoll 260 miles northwest of Madagascar. Aldabra is home to about 7000 land tortoises. Along with the 3000–4000 on the Galapagos Islands made famous by Charles Darwin, they constitute the total natural population of this giant reptile that once ranged over much of the southwest Indian Ocean. Aldabra is also home to the flightless rail and the pink-footed booby. Its unique ecosystem includes 12 endemic species or subspecies of birds and more than 18 of higher plants.

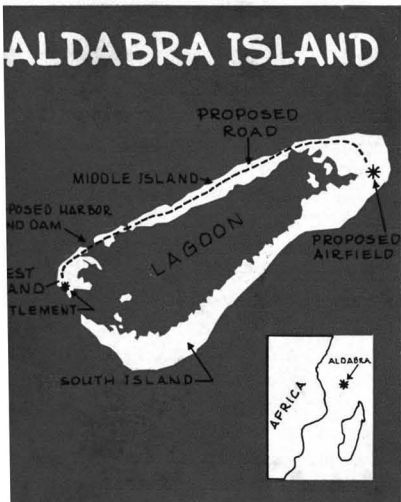
All this unique system is endangered by a proposal of the British Government to locate an airfield, a BBC transmitting station, and supporting facilities on the island. Britain's Royal Society has protested the proposal, pointing out how human intrusions have damaged other unspoiled ecosystems like Aldabra's. The United States' National Academy of Sciences issued a formal statement calling the plan "a threat of incalculable damage to one of the world's unique resources for scientific investigations." The Smithsonian Institution has also voiced concern over the plan.

Oceanic island

Aldabra is an oceanic island, possibly created by volcanic action followed by ages of coral growth. It has never been linked to continental masses. Un-

In reality, the argument boils down to whether our civilization is so money-oriented that to save a few dollars we are willing to destroy something unique and of permanent scientific and human interest. Would we destroy the Parthenon in order to use the Acropolis as a radar site, to save the cost of building an artificial platform? I hope not, but sometimes I wonder. If this is our philosophy we are destined to inhabit a progressively more impoverished world.

F. Raymond Fosberg, Smithsonian Institution, in *Atlantic Naturalist*



OUTLOOK

less man interferes, oceanic islands get their flora and fauna by immigration across the sea. However, many forms of life are poorly adapted for such immigration. So, except for bats, few land mammals have reached oceanic islands. Amphibia, freshwater fishes, and many orders of insects never appear.

An oceanic island may provide a haven for a species in trouble on the mainland from competitors or predators. It may develop its own plants and animals; flightless birds and insects may evolve, for example, if flying out to sea is dangerous.

Oceanic islands provide models or natural laboratories for the study of ecological and evolutionary problems. Indeed, Charles Darwin developed many of his fundamental ideas on natural selection from his observations of the simplified ecosystem of the Galapagos Islands.

Even among oceanic islands, Aldabra has special attributes:

- It is only 400 miles from Africa and so has had greater opportunity for animal and plant colonization than a more isolated island.

- It is an elevated atoll and so has a wider range of habitats than a sea-level atoll.

- It is relatively untouched by man. Lacking guano and phosphate rock, it has not been industrialized as have many other Indian Ocean islands.

The terrain is difficult and has never been considered suitable for cultivation. Apart from rain, there is little drinking water. Sporadic attempts have been made to develop the island. Currently, less than 100 contract laborers are on West Island; they live by cutting mangroves and coconuts, by fishing, and by turtling.

Why, then, put an airfield on this scientific treasure? The only reason, say the critics, is strictly economic. Aldabra is larger than other islands in the vicinity. Thus, it provides a cheaper site for building an airfield in what is considered a strategic location.

Conservation won't help

In trying to save Aldabra, the Royal Society is against half-way measures;



Sea bird. Great numbers of pink-footed boobies nest in the mangroves of Aldabra's Middle Island. The area also serves as the breeding grounds for the frigate population of the entire Indian Ocean area

"No amount of conservation planning and foresight could avoid the loss of the major contribution which the study of Aldabra can make to science—a contribution that can be made only by total preservation of the island for long-term studies."

The proposed development would affect the island community in several ways. The planned runway is slated for the breeding and browsing grounds of the tortoise. The large-scale clearing of vegetation would kill off some species of animals.

The lagoon that makes up the central part of the island would be dammed, affecting the ecology of the lagoon mangroves and the birds which now feed on the lagoon at low water. The frigate bird, with its penchant for hovering at low altitudes, would pose the same problem for aircraft as the albatross does on Midway.

A road will be built connecting the four main islands. When Aldabra was first colonized, various mammals, including goats, cats, and dogs, were introduced. They are now confined largely to the South and West Islands. The road will permit them to spread to Middle Island, with its large bird population. The flightless rail will be particularly vulnerable to the cats, and goats could mean the end of the vege-

tation on which tortoises depend.

Modern man also brings with him the problems of sewage disposal, insecticides, oil wastes, and aircraft noise. The result, the Royal Society feels, would be ecological chaos in what was once an unspoiled island ecosystem.

The final decision on Aldabra will be reached by May of 1968. Meanwhile, the Royal Society has mounted an expedition to gather as much information on the island as possible before the threatened construction starts. In the first part of the expedition, seven scientists spent five weeks on the island making a preliminary survey of numbers and distribution of animals and plants. They came back more convinced than ever that Aldabra should be preserved. The studies, which will continue to March 1968, will cover both terrestrial and marine ecology and will span both wet and dry seasons.

This is not the first time scientists have had to take up the cudgels in defense of Aldabra. In the 1870's, Charles Darwin and other scientists successfully opposed, at least for a while, a scheme to settle laborers on the island to harvest mangrove. Perhaps scientists again will be able to keep one small part of man's environment the way nature made it.

Water Management

A fashionable topic

In recent years water, water management, and water pollution control have all been headline news. Growing concern over water pollution plus recent droughts, particularly in the northeast, have helped make water management a fashionable topic. The concern over water problems is certainly justified. However, there are some fallacies in the publicity about the demand and supply of water.

The popular thesis that supply of water is fixed and that demand will soon outstrip supply makes the problem sound more ominous than it really is. It is true that the supply of water is fixed. In fact, the total amount of water available to the earth is relatively constant.

This fixed quantity of water constantly moves through the earth's natural water cycle. The water vapor in the air forms clouds from which it precipitates as rain or snow on the land or surface waters. Water falling on land areas either re-evaporates directly into the atmosphere, runs off in streams to the oceans, or seeps into the soil. The seepage from land and surface water either replenishes the underground water table or is returned to the atmosphere by transpiration from vegetation.

We are still learning how best to manage parts of the water cycle for the most advantageous use of the water available to us. Water management involves having enough water of necessary quality at the right place and at the right time. Some of the most important methods of water management are the following:

- *Flood control* seeks to keep streams at a maximum year-round level. Runoff is impounded during periods of high precipitation and melting of snow and ice. It is released during normal periods of low stream flow.

- *Weather control* attempts to control water supply by controlling the time and place of precipitation.

- *Pollution control* keeps water that has been used at a quality high enough to allow its use again by others, and to prevent spoilage of such natural resources as fish and wildlife.

- *Reuse by recycling* is largely practiced in industry. Cooling water is often recycled. Water is also used for different processes in sequence where each process requires water of lower quality than the preceding one.

- *Renovation* restores polluted water to sufficiently high quality for repeated use for the same purpose—for example, as potable water.

- *Desalination* of salt or brackish water provides usable fresh water from the vast quantities of saline water.

- *Geographic location of the user* can also be selected to take advantage of relatively remote supplies of water. We ship alumina vast distances to take advantage of low power rates for its conversion to aluminum metal. Similarly, we will begin to choose plant sites where low cost water is available.

By working with these management tools and expending the necessary funds, we can manage the fixed supply of water to meet the foreseeable demand. The methods used will depend on the combined factors of cost and effectiveness. In many instances no one method will suffice. Instead, combinations of methods will be used.

Dependable flow

An average of 4.3 trillion gallons of water falls on the continental U.S. every day. However, of this total more than 3 trillion g.p.d. are lost back to the atmosphere through evaporation and transpiration, leaving a net stream flow of 1.26 trillion g.p.d. This stream flow is irregular, alternating between floods and low water.

Through the best system of flood control that appears economically feasible, only about half of the average flow can be made available during the time

of lowest stream flow. Thus, the dependable minimum flow is only 630 billion g.p.d. Roughly half the stream flow is required for navigation, waste discharge, recreation, fish and wildlife, leaving the available supply for public, industrial, and agricultural use at only 315 billion g.p.d.

The total estimated U.S. intake of water for these purposes in 1965 was 356 billion g.p.d.—already more than the supply. Most of the water intake is returned to the cycle, although not always where it can be used again. Net consumption, the quantity not available to be reused, is 138 billion g.p.d.

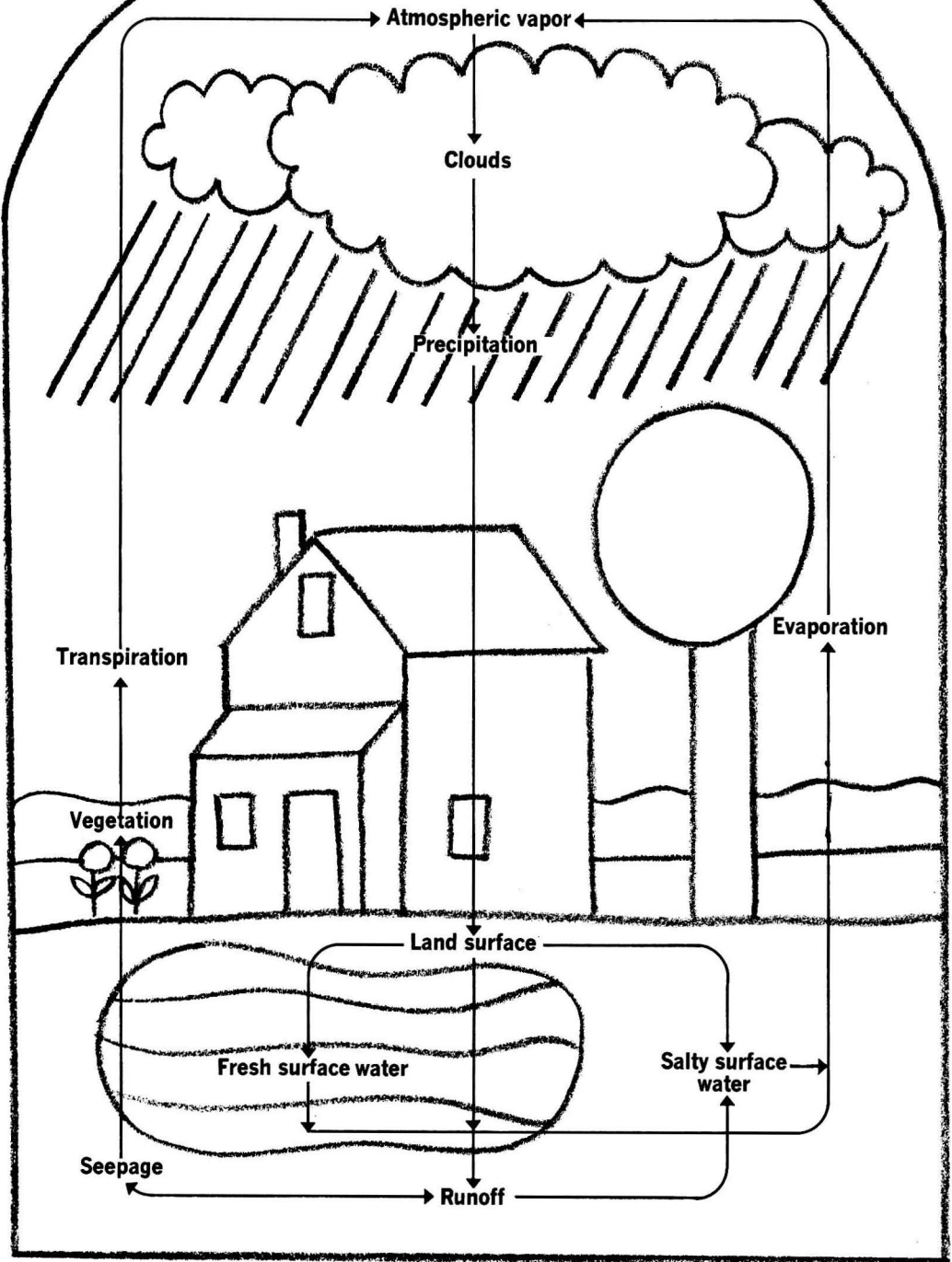
Irrigation requires more water—and consumes more water—than any other use. Instead of reentering the stream, most irrigation water is lost to the atmosphere by evaporation or transpiration.

Steam electric utilities are the next largest users of water. However, most of their water use is for once-through cooling, with most of the water returned to the available supply. Only about 1% is lost. The biggest use of water by manufacturing industry also is for cooling purposes. However, the net water consumption is close to 16%. Public water systems consume 22% of the water they take in, but rural domestic users consume 67%.

The total U.S. intake of water will grow at nearly 2.4% a year. Industry has the highest growth rate at 2.8% a year, followed by steam electric utilities and public water at 2.7% a year each. Use for irrigation is only expected to grow at 1.8% a year.

This article, the one following (page 785), and the three appearing in the September issue of ES&T (starting on pages 694, 698, and 703) were given in Chicago at the 154th ACS National Meeting during a symposium on Water Management sponsored jointly by the Divisions of Water, Air, and Waste Chemistry and Chemical Marketing and Economics.

**THE NATURAL
WATER CYCLE**



Gain in water reuse

In a survey of the market for chemicals in water and waste treatment recently completed by our company; one of the topics discussed at some 200 industrial plants was water reuse. A high percentage of the respondents indicated an increase in the amount of reuse of water. The recirculation ratio of water by industry from 1954 to 1964 has not increased as much as expected.

To date most of the recirculation by industry has been limited to cooling water, although some plants have started reusing process water, and a few have virtually closed systems requiring only small amounts of makeup water. The Kaiser Steel Co. mill at Fontana, Calif., has become an excellent, almost classic example of how water can be reused by industry. The Kaiser mill requires an intake of only 1400 gallons of water for each ton of steel produced, while the industry average is 65,000 gallons per ton.

As requirements to control pollution become more stringent, it will become increasingly more feasible economically to reuse water. The higher cost of water will also cause plants requiring large volumes of water to locate nearer cheap sources of water even though they may be farther from their raw materials, markets, or power sources.

Cost of water

The cost of water varies widely depending on the distance it must be transported, the treatment it requires, the use for which it is intended, and the source of the water. Ground water is cheapest, ranging from no treatment cost to about 20 cents per thousand gallons. However, drilling wells to tap the ground water may be prohibitively expensive. Fresh surface water is generally easier to get, but treatment costs run 20 to 40 cents per thousand gallons. Depending on the condition of the waste water and the degree of treatment it requires, the cost of renovation of water ranges from 20 to more than 65 cents per thousand gallons.

Desalination has received considerable publicity as a method for supplying water, but to date it is too expensive—\$1.00 per thousand gallons—for any but a few select locations where fresh water is at a premium. The city of Key

West, Fla., and the Guantanamo Naval Base in Cuba are two places where demand merits supply by desalination.

Thus, in areas where ground and surface waters are not available in sufficient quantities, water renovation and reuse go together to give the best means of assuring an adequate supply of water. Renovation includes restocking the ground supply with water for eventual

use as well as treatment for immediate reuse.

The cost of the various treatment processes ranges from a low of 0.5—1 cent per thousand gallons for ground-water spreading to more than 50 cents for wet oxidation. Most of these processes also require other treatment steps for renovation to high-quality water. To be economically feasible, the reno-

AVAILABLE U.S. WATER SUPPLY

Billion gal./d.

Precipitation.....	4,300
Evaporation and transpiration	-3,040
Net stream flow.....	1,260
Unusable floodflow.....	-630
Dependable minimum flow.....	630
Navigation, fish, wildlife.....	-315
AVAILABLE SUPPLY.....	315
ESTIMATED INTAKE, 1965.....	356
NET CONSUMPTION, 1965.....	138

U.S. INTAKE AND GROSS USE OF WATER FOR MANUFACTURING

Billion gal./yr.

Year	Total intake	Gross use	Recirculation ratio
1954.....	11,570	21,042	1.82
1959.....	12,131	26,257	2.16
1964.....	14,045	30,599	2.18

Source: Census of Manufacturers

ESTIMATED GROWTH IN INTAKE OF WATER IN U.S.

Billion gal./d.

	1965	1975	Av. annual increase, %
Irrigation.....	142	170	1.8%
Steam electric.....	111	145	2.7
Industrial.....	74	98	2.8
Public water.....	23	30	2.7
Rural domestic.....	6	7	1.5
	356	450	2.4%



D. R. Dykes



T. S. Bry



C. H. Kline

Donald R. Dykes joined *Charles H. Kline & Co., Inc.*, in 1967, having previously worked as an industrial engineer at the *New York Central System* and as a highway planning engineer at the *N.Y. State Department of Public Works*. Mr. Dykes received his Bachelor (1961) and Master (1967) degrees in Management Engineering from *Rensselaer Polytechnic Institute*. Mr. Dykes is a member of *Chemical Industry Association*.

Thomas S. Bry joined *Charles H. Kline & Co., Inc.*, in 1963, having previously worked as a research chemist at *Merck & Co.* (and later as assistant to the national sales manager of the food products department of that company). Mr. Bry received his B.A. from *Middlebury College* in 1958. He is co-inventor of many patented drug synthesis processes and author of articles on chemical markets.

Dr. Charles H. Kline is founder (1959) and president of *Charles H. Kline & Co., Inc.* Previously (1949-52), he was manager of product planning in the *General Electric* chemical division, then (1952-56) manager of the chemical development division of *Climax Molybdenum*. From 1956-59, Dr. Kline was scientific director at *Shulton, Inc.* He received his B.A. (1940) and Ph.D. (in physical chemistry, 1944) from *Princeton University*. He is a member, among others, of *ACS, AAAS, Society of Chemical Industry, Commercial Chemical Development Association, Chemical Market Research Association*.

vation of water to potable quality should cost no more than 30 cents per thousand gallons. Seven of 14 available treatment methods are in this range.

Where geological conditions are suitable, ground-water spreading is the least expensive water treatment method because the soil and rock serve as the basic treatment equipment, and little additional treatment is required. Water is stored naturally in underground aquifers. The added cost of pumping the water from the aquifer to the point of use is relatively low. Ground water injection in deep wells can also be an economical method of renovation, although a fairly high degree of pretreatment is necessary before the water is injected. This method, too requires special geological conditions, and the problem of getting the water back to the surface for reuse occurs in both methods of renovation.

Other methods of renovation are somewhat more expensive, but are preferred in most cases because the water remains available for immediate reuse. Tertiary oxidation ponds remove up to 60% of the biological oxygen demand (BOD) remaining after secondary

treatment. However, they require a large land area. Foam separation is particularly efficient in removing detergents and also removes some residual BOD.

Carbon adsorption removes up to 95% of total oxidizable organics and does not require a large land area. The recent introduction of granular activated carbon that can be regenerated by air oxidation should greatly extend the utility of this process.

Sand filtration following conventional primary and secondary treatment and tertiary coagulation and sedimentation removes up to 99% of BOD and suspended solids. Water renovated by this process requires only chlorination to bring it to potable quality. Coagulation and sedimentation alone remove up to 95% of phosphates and 70% of organic nitrogen.

The last eight treatment methods (electrodialysis, incineration, reverse osmosis, ion exchange, freezing, distillation, liquid-liquid extraction, and wet oxidation) are still in advanced development stage. Their costs range from 32 cents per thousand gallons to achieve water of potable quality by

U.S. INTAKE AND NET CONSUMPTION OF WATER, 1965

Billion gal./d.

	Intake	Net consumption
Irrigation.....	142	116
Steam electric.....	111	1
Industrial.....	74	12
Public water.....	23	5
Rural domestic.....	6	4
	356	138

AVERAGE COST OF TREATMENT OF SUPPLY WATER BY SOURCE

Water source	% Total		1965 ¢/1000 gal.
	1965	1980	
Surface fresh.....	> 80%	< 70%	20-40¢
Ground.....	15	15	0-20
Salt and brackish.....	0	< 5	100
Renovated.....	< 10	> 10	20-65

METHODS OF WATER RENOVATION AND THEIR COSTS

Cents per 1000 gal.

	Process only	Total for potable water
Ground-water spreading	0.5-1¢	15¢
Ground-water injection	5	20
Tertiary oxidation ponds	2-4	22
Foam separation	2	27
Adsorption on carbon	5-10	27
Sand filtration	0.7-4	28
Coagulation sedimentation	7-15	30
Electrodialysis	15-20	32
Incineration	20	34
Reverse osmosis	15-25	35
Ion exchange	25-29	40
Freezing	40	54
Distillation	45-54	62
Liquid-liquid extraction	50	62
Wet oxidation	54	66

Source: Richard J. Frankel, Resources for the Future, Inc.

ESTIMATED COST OF RECLAIMED SEWAGE EFFLUENT VS. ALTERNATE SOURCE

Cost per acre-foot

Location	Use	Reclaimed effluent	Alternate water supply
Texas.....	Irrigation	\$ 0	\$25-80
California.....	Irrigation	0-8	10-? ^a
Maryland.....	Steel mill	11	44
Texas.....	Refineries	14-16	44-45
California.....	Ground-water recharge	18	42
California.....	Park lakes	23	70
Texas.....	Power plant	24	92
Nevada-N. Mexico.	Golf courses	27-49	30-75

^a No good alternative available.
One acre-foot equals 325,850 gallons.
Source: Richard J. Frankel, Resources for the Future, Inc.

electrodialysis to 66 cents per thousand gallons for recovery of water by wet oxidation of sludge.

Each of the 15 treatment methods is in a different stage of development and each has limitations and special areas of application. Furthermore, new technology, or greater acceptance for any one may alter its costs considerably. In each case where the costs of renovating sewage effluent and the estimated costs of alternate sources of supply have been determined, there is ample evidence of a considerable saving by using the reclaimed effluent.

There are many other cases where sewage effluent has been reused for different purposes. One of the most noteworthy cases occurred in Chanute, Kan., where the town's regular water supply failed and sewage effluent was treated to provide the town with much of its supply of potable water. The main problem was a gradual buildup of inorganic salts, a problem which could be solved by ion exchange, electrodialysis, or reverse osmosis. There are psychological factors against reuse of sewage, but they can be solved.

In many cities the intake of municipal water is only a short distance downstream from the point of sewage discharge of another city. In other cities personnel in charge of municipal water prefer to transport good water long distances rather than treat polluted water that is available nearby. Examples of the two different philosophies are Philadelphia and New York City. Both have large but polluted rivers running past them.

Philadelphia has met the psychological problem successfully, while New York has avoided it. Philadelphia takes water from the nearby Delaware River and treats it thoroughly. New York builds dams and transports clean water more than a hundred miles through a series of reservoirs and aqueducts, but performs very little treatment.

The supply of water is fixed, but demand will not soon outstrip it. Water is virtually never consumed or removed permanently from its natural cycle. It is merely borrowed.

The cost of borrowing and using water will rise over the years and must be accepted as a cost of our rising standard of living. However, effective water management and modern technology can supply enough water of good quality to meet our needs for years to come.

Market for Water Pollution Control Equipment Burgeons

It hardly matters that there is no firm dollar figure on the water pollution control equipment market as it may develop in the next several decades—equipment makers are satisfied that it runs into the tens of billion dollars

A whole new array of elegant terms has appeared commensurate with the new status and scope that water supply and pollution control have assumed as a market of considerable eminence with expectations of significantly increased expenditures and potential growth.

Terms like sewage or sewage treatment and trade wastes are no longer preferred usage and are even frowned upon by practitioners in the field. The old expressions have been replaced by such terms as municipal or industrial waste water and waste water treatment, water management, environmental control, and the like. These new terms are much more palatable when one talks about large-scale re-use of "used" water, even municipal waste water, for residential, commercial, and industrial purposes.

The new look in phraseology is indicative of change and the acceptance that problems of water supply, water shortage, and water quality can no longer remain divorced from each other. Water resources planning must recognize that the ultimate economic, public health, and esthetic well being of the nation is dependent upon a close interrelationship of all aspects of water supply, water quality, and pollution control if a sustained yield of high quality fresh water is to be assured in all localities in the future. Upgrading and maintaining water quality and increased re-use of water by both industry and municipalities are the most attractive approaches to solving the problem. Ultimately, the only difference between water treatment and waste water treatment will be the source of supply, either used water discharged by others or one's own used water.

Existing technology and equipment permit closing the water circuit to produce potable quality water and water for most industrial uses. Although

present technology can be improved and optimized, the major barrier to closing water circuits is cost, which current estimates put at 40-60 cents per thousand gallons. This economic barrier will remain a serious impediment if we continue to underestimate the value of water as a basic commodity.

Market survey limits

In a consideration of equipment markets and marketing in water management it is necessary to define some of these terms if we are to limit the universe of concern in this market analysis. Water management is only one facet of environmental control. Water management can include resource development, power, flood control, water supply, pollution abatement, desalting—even swimming pools. This analysis in this article is limited to municipal and industrial bulk water supply and waste water treatment.

Equipment is limited to specialty equipment used for direct processing of water and waste water such as screens, flocculators, sedimentation devices, aerators, filters, ion exchangers, distillation units, degassifiers, deaerators, evaporators, digesters, incinerators, centrifuges, chemical feeders, chlorinators, and the like. The analysis does not include pumps, pipe, electrical devices, instrumentation, or equipment used to perform service functions in treatment facilities.

An overall market view

The major drought of the mid-sixties served to spotlight the nation's water supply and pollution predicament. It is now a major political issue which has accelerated federal intervention and legislation; but, to date, neither action nor funding. Few practitioners in the field would deny that acceleration is needed. Despite all past ac-

accomplishments, the backlog of treatment needs has continued to grow and the nation's waters have continued to deteriorate.

Estimates of expenditures needed to rectify the condition have been varied, generated by many sources, and involving substantial sums of money. Enough money, in fact, that water management has become a glamour market with federal participation likely to approach an order of magnitude similar to past interstate highway, atomic energy, and space programs.

Hanks and Kube (1966) predict the pollution abatement market will total at least \$275 billion through the next 34 years (to 2000). This total includes \$110 billion (\$3.2 billion per year) for water pollution control, \$105 billion for air pollution control, and \$60 billion for solids disposal. The Business and Defense Services Administration in a 1962 report placed construction requirements for water and sewage works for the period 1962-70 at \$39 billion. This report called for an annual average expenditure of \$4.3 billion during this period, more than double the record annual rate of nearly \$2 billion during recent years.

The Conference of State Sanitary Engineers reported the backlog of needs for municipal waste water treatment in 1966 at nearly \$2.7 billion. This figure has been criticized by many as too conservative on the basis of data from New York State alone (about 10% of the population) which concedes that by 1972 it must spend a total of \$1.7 billion for needs already identified. This figure, projected nationally, gives an annual expenditure of \$2.8 billion. The U.S. Senate Public Works Committee concludes that the cost of meeting treatment plant construction needs by 1972 would be at least \$20 billion. Other frequently quoted market estimates indicate a \$70-75 billion expenditure for the next 20 years, including at least \$30 billion for municipal wastes and another \$40 billion for industrial wastes. The U.S. Chamber of Commerce says industry's share of the bill for water pollution control will total \$32 billion between now and the year 2000 (approximately \$1 billion per year).

Engineering News Record reported that sewage treatment plants built in the U.S. during the past 10 years cost more than \$3.4 billion. Those built in

the five preceding years cost only \$890 million. Further, even using the most conservative estimate of the present backlog, it will cost the country close to \$14 billion through 1980—nearly \$920 million a year to meet all commitments.

Congress, in 1966, authorized \$3.8 billion in construction grants to municipalities through 1971. Assuming an average of 40% federal participation. Congress believes the expenditures required over the next five years should be at least at an annual average of \$2 billion per year. Although Congress appropriated \$450 million in construction grants for fiscal 1968, the Administration's budget request for municipal treatment plants is only \$200 million. The Administration contends that this is all that is needed right now since the Federal Government and the states are presently in the water quality standard setting stage. However, it is safe to assume that the lower budget request also reflects the government's present fiscal problems due to the Viet Nam War, inflationary pressures, and competition for funds.

Current attraction to the market by many profit-minded groups stems from

Construction Needs for Water and Sewerage Utilities, Public and Private, 1962-1970

(In millions of 1960 dollars)

Item	Total		Water Utilities		Sewerage Utilities	
	Total Volume	Annual Average 1962-70	Total Volume	Annual Average 1962-70	Total Volume	Annual Average 1962-70
To remedy present deficiencies.....	\$11,905	\$1,323	\$5,157	\$ 573	\$ 6,748	\$ 750
To offset obsolescence and depreciation.....	8,707	967	3,729	414	4,978	553
For growth.....	18,487	2,054	9,244	1,027	9,243	1,027
Total.....	39,099	4,344	18,130	2,014	20,969	2,330

Source: Construction Review, September 1962
Business and Defense Services Administration
U. S. Department of Commerce

the magnitude of the required expenditures quoted by the different sources. Beyond that, the variations encountered lead to confusion. Estimates of expenditures vary by more than 100%, the time factors considered are different, and, finally, the goals for water quality improvement are just now being formulated. A meaningful analysis of the specialty equipment market in water management as defined requires separating the wheat from the chaff, a recognition of significant market influences, and some basic assumptions.

Market influences

Present market stimuli stem from three sources: • A recognition of the deficiencies of the past resulting in a substantial backlog of construction needs for both the municipal and industrial segments of the market. • The desire to upgrade water quality generally. • The realization that used water must become an increasingly important source of supply if future demands for fresh water are to be fulfilled.

Additional influences will be population growth, industrial growth, changing water use patterns, and the value of

the dollar. These influences affect the various segments of the market differently. The waste water treatment market will grow at a faster rate than the water treatment market, and the industrial market will grow at a faster rate than the municipal market. Substantial improvement in water quality may even have a depressive effect on the water treatment market as it exists today.

Eventually, differences in water and waste water treatment facilities might cease to exist and they will become one treatment facility. A single, hybrid plant will evolve using waste water unit operations and processes for primary and secondary treatment and water unit operation and processes, and others, for tertiary and advanced waste treatment. This analysis assumes that such an evolution will not occur within the next 10 years but could become a reality before the end of the century.

Additional assumptions are: • Water quality standards will require an average reduction in pollutants attainable by secondary treatment, or an equivalent treatment in terms of reduction efficiency, during the next 10 years. • No significant technological breakthrough will occur which will

materially change processes now in use or under development. • No undue delay in the program will be caused by such outside influences as domestic and international or economic problems.

Municipal equipment market

A review of past performance often yields clues which can assist in the risky market projection process. Construction data for municipal water supply and waste water disposal projects for the period 1960-66 have been prepared. These data establish the lack of significant growth in waste water treatment and even point to the stagnation in facilities construction which is responsible, in part, for the present water dilemma. The Federal Government must share the blame because of the very elusive carrot it held out to local governments in terms of construction grants prior to 1966.

Water treatment. Actual construction contracts in 1966 totaled nearly \$710 million and exhibited an average annual growth rate of 7% for the previous five years. Aside from population growth, factors which contributed to this progress were increase in population served by water utilities and a

**Summary of the Backlog of
Municipal Waste Water Treatment Needs, 1966**

<u>Source or Problem</u>	<u>Facilities</u>	<u>Population Served (Millions)</u>	<u>Estimated Cost (Million Dollars)</u>		
			<u>Plants</u>	<u>Ancillary Works</u>	<u>Total</u>
Untreated discharges.....	1,288	6.8	\$ 437.0	\$ 349.6	\$ 786.6
Inadequate treatment.....	1,697	24.6	552.8	487.4	1,040.2
Sub totals.....	2,987	31.4	989.8	837.0	1,826.8
Potential sewage from unsewered communities.....	2,668	6.2	468.0	374.4	842.4
Totals.....	5,653	37.2	1,457.8	1,211.4	2,669.2

Source: Summary Report, 6th Annual Survey of Municipal Wastes Treatment Needs by Conference of State Sanitary Engineers, January 1966

Water Management Market 1966-1967

(million 1966 dollars)

	Total Construction Value		Treatment Facilities		Equipment	
	1966	1976	1966	1976	1966	1976
Municipal Water.....	\$ 710	\$1,450	\$150	\$ 440	\$ 30	\$ 90
Municipal Waste Water..	1,050	2,300	400	1,200	64	220
Industrial Water.....	280	420	180	275	40	65
Industrial Waste Water..	240	570	190	450	57	160
Total.....	2,280	4,740	920	2,365	191	535

Construction Data Reported

Total Actual Contracts⁽¹⁾— Million dollars

Year	Water Supply	Waste Water Disposal
1966.....	710 ⁽²⁾	1,000 ⁽²⁾
1965.....	691 ⁽³⁾	860 ⁽³⁾
1964.....	654	910
1963.....	590	1,084
1962.....	507	865
1961.....	573	829
1960.....	645	718

⁽¹⁾ USPHS Pub. 758

⁽²⁾ ENR forecast

⁽³⁾ ENR data

backlog of inadequate facilities amply demonstrated by the fact that during the recent drought there was not only a shortage of water but also evidence of a shortage of water planning, particularly among municipally owned utilities.

By far, the greatest percentage of construction dollars goes to source of supply, transmission, distribution, and storage. Water treatment facilities consume only about 20% of construction dollars which would amount to almost \$150 million in 1966. The specialty equipment portion of this package amounts to about \$30 million.

The growth rate between 1966-76 is expected to average 7%, indicating total construction expenditures of \$1.45 billion by 1976. Of greater significance to equipment manufacturers is that the percentage of construction dollars for water treatment facilities will increase. This will be the result of the desire by the water treatment industry to improve the quality of its product. In 1976 water treatment facility expenditures will total \$440 million and specialty equipment \$90 million.

Waste water treatment. In 1966, municipal waste water construction contracts came to more than \$1 billion.

Treatment facilities accounted for almost 35% of the total or \$400 million and specialty equipment close to 16% of treatment facilities or about \$64 million. For the next 10 years a growth rate of 8% per year is anticipated, indicating a construction volume of \$2.3 billion in 1976. Again, of greater consequence, is the expectation that treatment facilities and specialty equipment will gain an increased share of the market because of higher water quality requirements. Most new plants will be secondary treatment plants and many existing primary plants must be upgraded to the secondary efficiency level.

Expenditures for treatment facilities will increase to \$1.2 billion (specialty equipment to \$220 million) in 1976.

The equipment portion of the municipal treatment facilities market has varied from 13 to 16% annually. Two recent developments which have upset this ratio are the stabilization pond and the package waste water treatment plant. The specialty equipment manufacturer obtains zero percent of the stabilization pond market and 40-60% of the package plant market when the steel tankage is included. Since their inception in the mid-50's, both types of treatment facilities have exhibited an annual growth rate of 10-14%, far above the industry average. In 1965, each accounted for a construction volume close to \$11 million.

Industrial equipment market

The industrial segment of the market is, and always has been, difficult to assess. The market includes influent treatment, in-plant processing, cooling, and special treatments to produce a variety of specification water. Estimates of the total industrial water management market in 1965 range between \$300-650 million. Data reporting the equipment portion of this market falls between \$50-125 million. As would be expected, equipment obtains a larger share of the treatment facilities market which, in turn, also represents a larger percentage of total construction volume.

Water treatment. A survey of all existing data for water treatment indicates a total capital expenditure of close to \$280 million, including \$180 million for facilities (\$40 million for equipment). Growth rate is expected to follow industry average of 4%. Such a growth rate would increase total expenditures to nearly \$420 million in 1976, of which \$275 million would go for facilities (\$65 million for equipment). No significant changes are expected in this market except that the growth rate could be slowed if a substantial improvement in water quality is achieved.

Waste water treatment. Total capital expenditures for waste water treatment in 1966 were estimated to be nearly \$240 million, of which \$190 million

Waste Water Treatment Processes Most Frequently Mentioned by 2162 Respondents

Process	Number of Installations
Screening.....	316
Sedimentation and lagooning.....	933
Centrifuging.....	12
Filtration.....	39
Flotation (air and gravity).....	237
Flocculation.....	22
Chemical oxidation or reduction....	88
Emulsion breaking.....	11
Distillation and stripping.....	49
Evaporation.....	20
Incineration.....	77
Chemical coagulation.....	46
Neutralization.....	414
Biological oxidation.....	148
Anaerobic digestion.....	50
Wet oxidation.....	10
Stabilization Ponds.....	150
Other.....	207
Total.....	2,829

is for facilities (\$57 million for equipment). The rate of increase is expected to more than double industry average growth or to be at least 9%, indicating total capital spending of \$570 million in 1976 of which \$450 million is for facilities (\$160 million for equipment). Even at this rate of spending it will take industry 20 years to eliminate the backlog and provide treatment for all waste water discharges at secondary treatment efficiency levels.

A relatively high percentage of this industrial waste water market will shift over to the municipal segment because

of an increasing tendency to go into joint treatment in plants owned and operated by municipalities. In-plant process change in lieu of terminal treatment will increase. This increase should not, however, change the outlook for equipment appreciably in the total market.

Processes and equipment

The municipal field has been accused of propagating a relatively low level, old technology in its approach to water and waste water treatment. To a degree this is correct because the em-

WATER TREATMENT PROCESSES ■ EFFECTIVENESS AND COST

PURPOSE	PRIMARY TREATMENT	SECONDARY TREATMENT	TERTIARY TREATMENT	QUATERNARY TREATMENT	SLUDGE DISPOSAL	SPECIAL TREATMENT
	Removal of gross & fine solids, partial removal of suspended solids, reduction in BOD & grease removal.	Further removal of suspended solids & BOD; nitrification in some cases.	Effluent polishing & residual BOD removal.	Removal of all color viruses & bacteria with salt removal as required.	Disposal of organic or inert sludges.	Various—to meet special requirements on specific wastes.
PROCESS OR EQUIPMENT INVOLVED	Grit removal, screening, grinding, sedimentation & flocculation.	Trickling filters & clarification or aeration & clarification.	Flocculation & sedimentation or carbon treatment.	◄ Membrane separation ◄ Ion exchange for salt removal.	◄ Sludge Drying Beds ◄ Digestion ◄ Drying ◄ Burning ◄ Thermal Oxidation	◄ Chlorination ◄ Chemical Treatment ◄ Evaporative Cooling ◄ pH Adjustment (Chem.) ◄ Ion Exchange ◄ Evaporation ◄ Freeze Concentration ◄ Solvent Extraction ◄ Fluid Techniques
EFFICIENCY OF REMOVAL	BOD 30-40% SS 50-75%	85-95% 85-95%	90-100% 98-100%	Removal of trace organics.		Varied—depending on process & application.
POLLUTION FACTORS ATTACKED OR CONTROLLED						
MICROBIOLOGICAL						
Bacteria						Chlorination
Virus						Chlorination
Algae & Aquatic Growth						Chemical Treatment
PHYSICAL						
Suspended Solids (Inert)						
Color						Chemical Treatment
Temperature Increase						Evaporative Cooling
BIOCHEMICAL						Chemical Treatment
CHEMICAL						
pH Level						pH Adjustment (Chem.)
Salts						Evap.-Ion Exch.-Freeze Conc.
Toxic Substances						Solvent Extraction
Radioactive Elements						Ch.Tr.-Sol. Ext.-Ion Exch.-Fl. Tqs.
Eutrophication						Chemical Treatment
WHERE APPLIED						
DOMESTIC SEWAGE						
INDUSTRIAL WASTES						Chem. Treat.-Chlorination ^a
Food						Chemical Treatment
Chemical						pH Adjustment (Chem.)
Textile						Chem. Treat.-Ion Exch.
Pulp & Paper						Chem. Treat.-Fl. Tqs.
Mining						Chem. Treat.-Ion Exch.
Petroleum						Chem. Treat. & Others
Metal Finishing						Chem. Treat. & Others
Atomic						Ch.Tr.-Sol.Ext.-Ion Exch.-Fl. Tqs.
TREATMENT COSTS (Per 1000 Gallons)						
DOMESTIC SEWAGE	3-4¢	5-10¢	1 Flocc. & Sed. 4-6¢ 1 Carbon Treat. 8-10¢	10-40¢	1-4¢	Widely Varied
INDUSTRIAL WASTES	2-5¢	2-20¢		10-40¢	1-50¢	

The shaded bars indicate the pollutants attacked in each of the treatment steps and the types of wastes to which each step may be applied. Also, the treatment costs for each category are approximate and are not cumulative horizontally.

POTENTIAL MARKET (Backlog)

^a 1 Billion

^b 2.5 Billion (Depending on amount of water recirculation)



T. W. Lesperance is special assistant to vice president, North American Operations, Dorr-Oliver, Inc. He received his B.S. (1950) in chemical engineering from Bucknell University (Lewisburg, Penna). Previously (1950-52), he was an engineer with Kellex Corp., and from 1952-53 an engineer with Vitro Corporation of America. From 1954-63, Mr. Lesperance was technical specialist for industrial waste treatment with Dorr-Oliver, Inc. From 1964-66, he was associate editor of *Water and Wastes Engineering*.

phasis has been placed on construction of facilities and not on process or operation. The mere existence of a treatment plant, however, does not guarantee a solution to a pollution problem. Many treatment plants are not operated as efficiently as they could be operated and, as a result, some construction dollars are wasted. This does not mean that the basic technology in use is wrong. Such a plant, however, can be modernized and better operated to improve efficiency at reduced cost.

An accompanying chart summarizes the technology now in use in the waste water treatment field, where it is applied, its effectiveness, and its cost. A substantial degree of generalization is necessary to compress the volume and complexity of the information presented. The chart does not give precise or detailed answers to specific waste treatment problems. It does provide a broad and reasonably comprehensive picture of the state of the art. The National Association of Manufacturers and two other groups published (1965) the results of a survey of treatment processes most frequently used by industry, showing the technology now in use and relative frequency of usage.

Market trends

Existing technology will become more sophisticated and new technologies for advanced treatment, such as desalting type processes now under study, will increase the equipment manufacturers' share of the total market. Hopefully, in the near future, process and plant operation will be given the consideration it deserves. A greater use of chemical treatment, instrumentation, and automation is needed.

The nutrient problem, even higher water quality standards, and greater water re-use will dictate an increased use of tertiary and advanced waste treatment which will enlarge the market potential even further. Water and waste water treatment plants will become more similar and eventually may become one. The future is promising. Let us hope that the present impetus will not be eroded by factors beyond our control. The needed acceleration, elimination of the backlog of needs, higher water quality standards set and met, and water re-use can solve the nation's water problems for years to come.

QUOTE . . .

TIME TO DEVELOP AN URBAN LAND POLICY

Suburbia is too often characterized by instant-blight commercial districts, torn and eroded land, wasteful and destructive water use. There is too much housing built on potentially disastrous flood plains, and Chinese Wall highways isolate and fragment too many neighborhoods. Open space is seldom planned and natural recreation sites too often disappear beneath subdivisions and highways.

We have treated land as an inexhaustible resource for urban use and have failed to translate the lessons of agricultural land policy to the environment of nearly three quarters of our people.

Finally, we have failed to link our cities, with their traditions and unique vitality, to the developing suburban communities.

But this is not all we find in suburbia. It would be foolish not to recognize the great achievement of our homebuilding industry during the last two decades. While we did not realize the optimum, our progress toward better housing was phenomenal. And we must not forget that in these sprawling urban areas the majority of our people live in a far better habitat than they ever did before. It is only the disadvantaged, many of whom live in urban and suburban pockets of poverty and ghettos, who find a greater gap between their aspirations and what they have acquired than they found a generation ago.

It is time now to develop an urban land policy, and an urban conservation ethic, comparable to that which we practice on farm and forest.

We cannot do this only on the federal level, or only on the state level, or only on the level of local government. There must be a partnership of effort and accomplishment among all these levels of government and with the private sector.

For all of us—public official and private entrepreneur—there is an overriding responsibility to the land itself. This is not only in the relationship of man to nature, although that is part of it. It is in consideration for the people who will occupy that land.

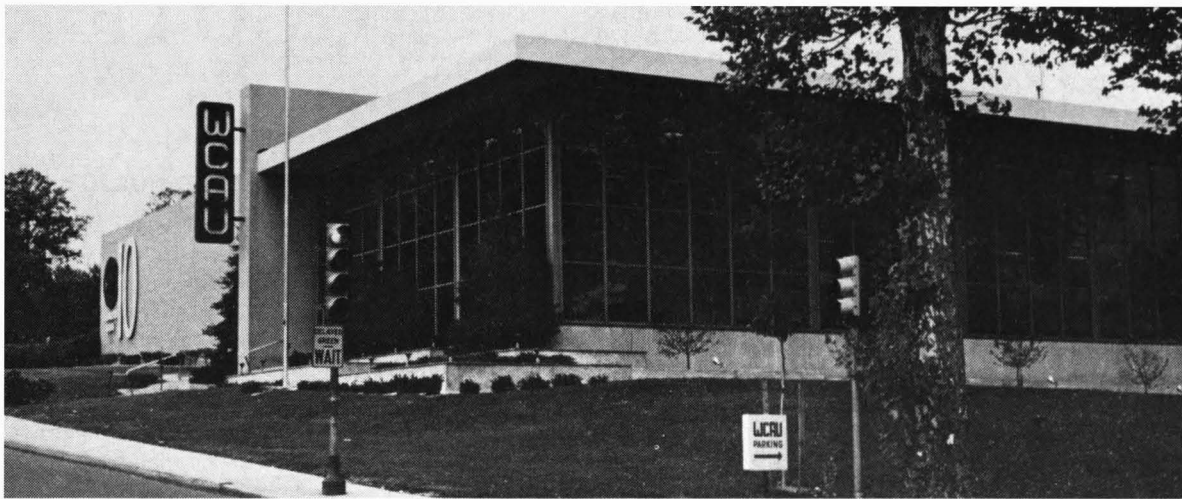
The land has always seemed endless, and we have ripped and torn and left devastation behind, and now we are paying for it. We will go on paying in the coin we cannot afford—wasted human resources—unless we begin to control our urban destiny.

Each of us has his area of responsibility for the land, and we cannot shirk that responsibility on any level. Our whole endeavor must be to bring man and land into harmony, to bring profit into harmony with good land use.

Most of the means are in hand to do this. What we must have is more commitment, more common will, and more political action to use these means, and quickly.

ROBERT C. WEAVER

Secretary, Department of Housing and Urban Development at a conference on "Soil, Water, and Suburbia", Washington, D.C., June 15, 1967



Radio Station Fires a Broadside at Regional Air Pollution Problems

superficial at times, dramatic at others, now casual, then serious, the station's talk show and their guests helped create a climate of awareness of the seriousness of air pollution in the Philadelphia area and for the need to do a vague something

engineering. WCAU's Barry Bricklin, psychologist and staff announcer Dan Curtis (right) chat with Noron (foreground), manager of human engineering, Bur Corp. The talk revolves around taking a systems ap-

proach to the creation of an environment in which human can live and work effectively. At incipient levels of contamination of the air there is evidence that the highest level human function are affected, Olson notes



OUTLOOK



Start-up. Producer Elisa Dorfsman confers with lead-off man, Bill Bircher, about the day's program on air pollution

"WCAU, good morning. It's 6:00 A.M., October 6, 1967." And with that, the Philadelphia radio station's full day devoted to air pollution got underway. While not quite unique in the station's broadcasting history, the full day's programming on a single subject is almost so. The subject:

Air Pollution—Danger Point. The audience: three quarters of a million people in the metropolitan area.

Bill Bircher, the lead-off man, for three hours interspersed commercial messages, traffic reports, weather, news, recorded music, and prepared editorials with comments promoting

the interview and discussion programs set for the remainder of the day. He took a few phone calls "dealing with pollution at the personal level—leaf burning, trash disposal, polluted streams—handling the calls in a serious but not lugubrious manner."

After a two-hour break for some network programs, this Columbia Broadcasting System affiliate got down to the serious business of the day: interviews, discussions, questions, answers, and lots of talk. The roster of participants included politicians, housewives, physicians, environmental engineers, chemists, leaders of citizen groups. Pennsylvania's Governor Shafer couldn't make it at the last minute, nor could Sen. C. Boggs (R-Del.). But a conference call was set up and Sen. Muskie (R-Me.) talked about the federal role in pollution control after which he fielded some questions asked by listeners. Also on the conference phone during the day was Dr. R. A. Prindle, assistant surgeon general of the U.S. And the talking went on.

Most of the conversation dealt with the health effects of air pollution, the problems involved with controlling air pollution, who's to blame for air

Conference call. Al Ringler (left), editorial director, and Donald Barnhouse (right) listen along with the radio audience as Sen. Muskie details by telephone the extent of the federal involvement in pollution control



WCAU 121 EDITORIAL

This transcript of a broadcast editorial defines WCAU's position on this issue. It is a matter of community importance. We hope you will take the time to read this transcript. We will be glad to consider requests for time for the expression of differing points of view. Your thoughts on the subject, pro or con, of course, most welcome at WCAU.

JOHN O. DOWNEY
Vice President, CBS Radio
General Manager, WCAU

SUBJECT: Inspection of Auto Pollution Devices Still Not Resolved
BROADCAST DATE: October 6, 1967

For several years, WCAU Radio has been calling on Pennsylvania State Legislators to make mandatory the checking of anti-pollution devices on automobiles.

The measure was passed unanimously in the State Senate and has the approval of Governor Shafer. But it is bogged down in the House, and has been for several months.

The bill was sponsored by Senator Edward G. Holl of Montgomery County after hearing a WCAU Radio demand for such action. And he says the measure is sure of passage if it ever gets to the floor for a vote. But the measure apparently has been pigeonholed in the Motor Vehicle and Highway Safety Committee. There are reports from Harrisburg that vested interests oppose the legislation.

The interests are not, as one might suppose, the auto makers. Senator Holl says he has the full support of car manufacturers. For the past several years all new cars sold in Pennsylvania have come equipped with crank-case breathing devices. They eliminate about thirty-three percent of poisonous hydro-carbons which have produced cancer in animals. But if they are not properly maintained, they emit more pollution than ever.

WCAU Radio intends to continue its fight for mandatory inspections until this particular rat-hole in the fight for cleaner air is plugged up. That is why we call on the Motor Vehicle and Highway Safety Committee to get moving and clear this bill for House action. The representatives of the people must have a chance to vote on it. And WCAU Radio believes no interest is bigger than that of the people who demand cleaner air.

####

#67-61

pollution, what is being done, and by whom. And the talking went on.

What was probably the most dramatic event of the day was the comment (at almost midnight) by Dr. William Rongaus, Donora, Pa., practicing physician in that small community since before the deadly pollution episode of 1948. To him the episode was not something that could happen. It was something that did happen. Nonetheless, he noted, at the time of those fateful hours, and to this day, there are those residents who deny the existence of the episode—or even that they were in it. Why? Probably, a peculiar fear of what could be severe economic consequences if local industry moved out.

Coordinated by producer Ken Artis, publicized by information director Hugh Ferguson, and with the blessings of general manager John Downey, the day long effort made a mild impact on the regional scene. It helped focus attention on the regional nature of a mounting air pollution problem. It got people involved. It added to the total awareness level. Yet, it accomplished little in actual fact. But the talking goes on.

Editorial. Read at regular intervals throughout the day, this editorial becomes another addition to a four-year-old and still growing portfolio of calls for action in the air pollution fight



WCAU RADIO CENTER THE CBS OWNED RADIO STATION IN PHILADELPHIA

Hi! If you have found me, we would appreciate your furnishing the information requested below and returning the card as soon as possible to assist us in completing a survey. Thank you!

Name: _____

Address: _____

Date & Time Balloon Was Found: _____

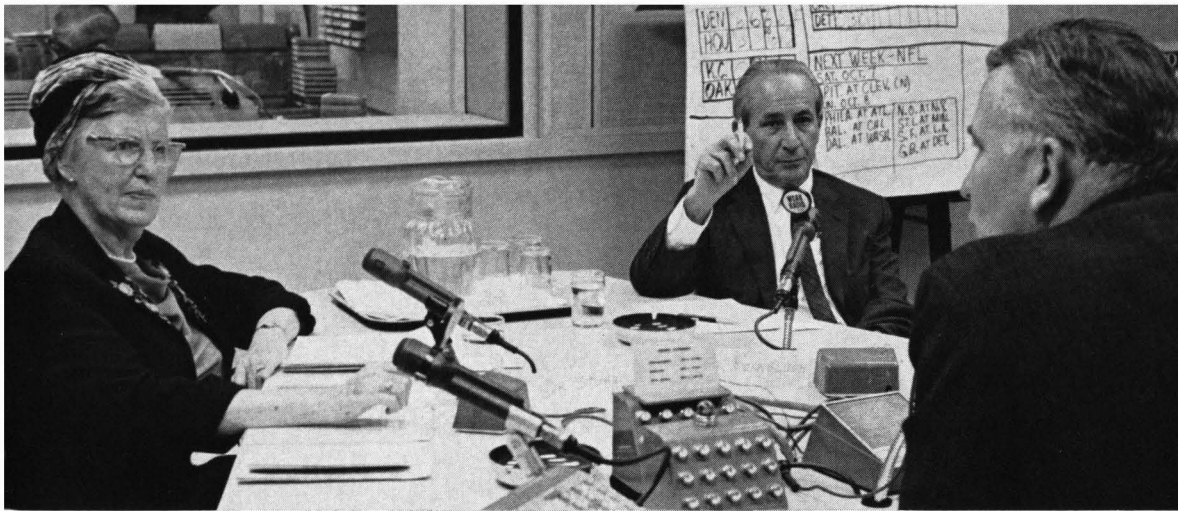
Location Where Balloon Was Found: _____

Other Interesting Circumstances?: _____



Regional. "Talk of Philadelphia" host, Ed Harvey (left to right) joins guests W. E. Jackson (chairman of the Jaycee air pollution committee and research associate in environmental engineering at Drexel Institute of Technology), H. C. Wohlers (associate professor of environmental sciences at Drexel), I. M. Levitt (chairman, Air Pollution Control Board of Phila-

delphia and director, Fels Planetarium, Franklin Institute), and J. O. Downey (general manager of the station) in releasing helium filled balloons from station roof. Each of the 500 balloons released carries a return post card questionnaire. Data from the returned cards will be used to demonstrate the need for a regional approach to air pollution problems



Scare, then fact. "It's murder—you just can't make it any more plain than that. Philadelphia is a murderer, and its weapons are polluted, foul, filthy air from industry, from your car, and, this Fall, from your own backyard. And just as sure as you are listening to me now, you and I are contributing to serious illness and possibly death through our own contribution to air pollution." So said Ed Harvey (right) as he got ready to introduce guests Dr. Katherine Boucot Sturgis (left), president elect of the Philadelphia County Medical Society

and clinical professor of medicine, Women's Medical College Hospital, and Dr. Igho H. Kornbluh (center), founder of the American Institute of Medical Climatology, vice president of the International Society of Medical Hydrology and Climatology, and chief of departments of physical medicine and rehabilitation at Northeastern and Frankford Hospitals. Once the audience's attention was gained, Harvey and guests settled down to a reasoned discussion of the facts of air pollution and its effects on living creatures



Panel. Moderator George Lord (right) establishes a solid base for 2½-hour open forum between radio audience and panel of experts, one of whom is Robert Goldberg (left), director of the Delaware Valley Regional Control Project



Donora revisited. Dr. W. Rongaus (left), resident physician at Donora, Pa., since before the tragic episode of 1948, Bruce Hogarth, then regional representative of region three, which encompasses Donora, and now with the National Center for Air Pollution Control, and Jack McKinney (back to camera), host of "Night Talk," relive some of the events of those terrible hours 19 years ago when the silent, deadly smog struck the small community

Air Pollution Studies Aided by Overall Air Pollution Index

Despite the value of an overall air pollution index in helping to determine the severity of an air pollution problem, the index must not be subverted to make the problem seem less complex than it is, nor hide gaps in knowledge

The problem of air pollution embraces all the undesirable effects—on men, animals, plants, and materials—of various waste substances in the air. These effects include corrosion and soiling of materials, poor visibility, unpleasant odors, detrimental effects on health, and fatalities. It is an extremely complex problem and many of the phenomena involved are inadequately documented and even less well understood at present. It is a very urgent problem, however, and remedial action must and will be attempted even without complete knowledge on which to base such action. Careful measurements are urgently needed to develop at least a background of empirical data as a guide to future action and, hopefully, to fill in some of the gaps in understanding which exist today.

Air pollution indices

Air pollution can be described in terms of a list of the concentrations of the presumably undesirable substances, usually man-made wastes, present in a given sample of air. This is in essence a catalog, not a simple definition. Because it is difficult to deal with such a complex concept, it

is common practice to try to find some sort of overall index of air pollution that can be expressed as a single number. This is reasonable and helpful, provided the index is not used to make the situation appear less complex than it is, nor to hide gaps in knowledge.

The evaporation of volatile liquids such as the thinner in paint or cleaning solvents, the discharge of gaseous wastes from industrial processes, and other non-combustion sources can and do contribute to the amount of pollutants to the atmosphere. There is ample reason to conclude that, in general, this amount will be quite small compared with that produced by combustion processes in automobiles, industrial plants, public utilities, space heating, and refuse burning which, according to Public Health Service data, exceeds 150 million tons per year of carbon monoxide, sulfur dioxide, oxides of nitrogen, hydrocarbons, and various airborne particles. Inasmuch as the major source of pollutants, therefore, seems to be combustion, and since it is clear that the concentration of these pollutants at any given time and place will depend on the degree of dilution by small-scale atmospheric turbulence and winds, a reasonable place to start

in searching for a general index of air pollution would be to divide a number which represents an amount of fuel burned by another number which represents the volume of ventilating air into which the combustion products of that fuel have been dispersed. The result can be expressed as tons of fuel per cubic mile of air and is referred to as the Combustion Products Index (CPI).

The number of tons of combustibles burned in a city can be obtained by a physical survey. This is laborious and complicated but the basic idea is simple and direct. The data on coal, oil, and gasoline deliveries as reported weekly by wholesalers can give estimated daily consumption with modifications based on degree-days. On gasoline, an allowance will have to be made for gasoline purchased outside the city but burned in the city. If a municipal incinerator is used, the data are, of course, available. Power plant use of coal, oil, or gas is accurately known. The quantities of industrial process material combusted will be a less direct measurement but stack measurements on typical processes will furnish a basis for reasonable estimates based on the bulk of material

T. A. Rich

General Electric Research and Development Center, Schenectady, N.Y.

handled. This is no easy task but when combined with the usual licensing and inspection procedures will furnish the most vital factor in air pollution—a measure of the total combustion which produces the bulk of pollutants within the city.

The volume of air in which the production products are mixed is simple in concept but may be extremely complicated in practice. As an oversimplified example consider a city, ten miles across, with a 5 m.p.h. wind and complete mixing to a height of 0.3 mile. The combustion products leaving the city would then be mixed in $10 \times 0.3 \times 24 \times 5 = 360$ cubic miles of air per day (see Fig. 1).

A CPI of tons/cubic miles is an average in time and, of course, applies only over the downwind boundary and under the meteorological conditions cited. It takes no account of control measures that might be specified (such as sulfur limitations in coal, changes in combustors, filtering attachments, and the like). In a limited way, however, it is a general indication of potential pollution in the city.

Outside sources

If data are available on sources of pollution outside the city, these can be added, with appropriate atmospheric dilution factors, to the general CPI for the city. Furthermore, the CPI concept can be sharpened to represent the total air pollution at any given point at a specific time. In this case a mathematical model of the atmospheric conditions and the com-

bustion sources is required. Large concentrated sources would be represented by a point source, major highways by line sources, and homes, offices, and minor highway traffic by area sources. Each of the sources will have to be estimated in some cases; however, the weekly average from the survey of combusted materials will help keep the estimates within reasonable limits. The exhaust from a point source spreads both laterally and vertically with distance from the source due to the turbulence in the wind. By taking all of these factors into account, it is possible to calculate an approximate overall value for the amount of combustion products which have been mixed with the air passing over any given point at any given time.

In theory it would be possible to calculate the concentration of a specific pollutant at any point in the city from the model described. With knowledge of the sulfur content of the fuels, for example, a number representing the generated amount of SO_2 for each source could be derived. However, some pollutants, like SO_2 , can react with other gases, be adsorbed on surfaces, dissolved in water (water absorbs some two hundred times its own volume of SO_2), and converted by sunlight to SO_3 . The amount of SO_2 lost in transit is not accurately predictable. Thus, in practice, calculations of specific pollutant concentration would be far from precise. The model itself is an approximation, meteorological data are notoriously variable, and other necessary parameters are difficult to obtain!

Representative samples

On the other hand, the measurement of the actual concentration of a specific pollutant at a point can usually be done with fair accuracy. The determination of a representative average over an area is a bit more difficult. The location at which measurements are to be made must be selected with care and a check made that concentrations measured there are really representative of the area. Specific pollutants will have to be measured in any event and one or more can be used to check the model.

For example, as a first approximation the SO_2 (due to coal) at a point would be a constant K_c times the part of the CPI at that point attributable to the combustion of coal. The constant factor K_c would be the same anywhere in the city. There would be similar factors for oil, gas, gasoline, refuse, and industrial processes. In this simplified example there are, then, six constants to be determined so that six independent measurements of SO_2 (at six different times or places) would be required to evaluate all of them. The same process would be required for other easily measurable contaminants.

Obviously it would be carrying optimism much too far to suppose that only six measurements for each of a few specific contaminants would be enough to validate a model of atmospheric pollution for even a small city. Application of statistical methods to a large amount of data will be required and achievement of consistent results will be a formidable task. Suc-

cess, however, would lead to a model that would dependably predict, for any given circumstances, not only the total products of combustion mixed with the air at any desired point in the city, but also the relative contributions of the various sources.

Control measures

Control measures can be costly in terms of inconvenience and money and their effectiveness must be evaluated to be sure the results will be worth their cost. The model can be improved as the day by day measurements are checked against results calculated from the model so that any proposed program can be evaluated on a computer before actual trial. Changes in traffic patterns, location of new industries, fuel restrictions, and the like are examples of long term programs. The model's ability to predict instantly the pollution levels that would be reached under the current conditions would be an invaluable asset in taking the proper control steps during inversions.

Specific pollutants

When it becomes possible, by a combination of measurement and modeling to prepare reasonably accurate daily, or perhaps even hourly "maps" of the concentration of specific atmospheric contaminants covering the major part of a city, these data can begin to be used as a starting point—for example, in public health studies—to determine the relative seriousness of the individual contaminants from various points of view, identify the worst offenders, and establish a basis for predicting certain types of damage.

Unless such studies are made with great care, however, there is a possibility of misleading results. This possibility was pointed out by Dr. Patrick Lawther of Saint Bartholomew's Hospital, London, in a statement made in 1955.

"The 1952 smog, like so many disasters, was much better documented than it was observed," he noted, "and

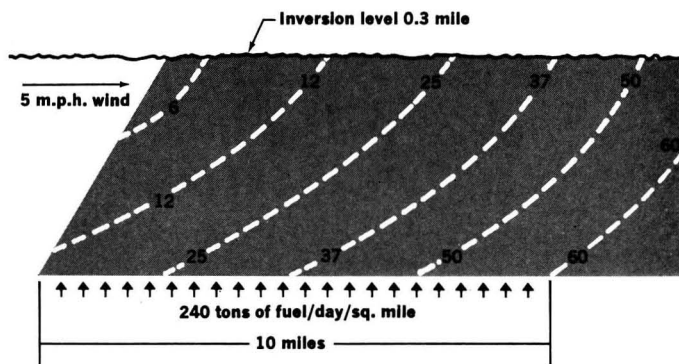


Figure 1. Combustion Products Index (CPI) in a hypothetical city 10 miles square. Total ventilating air—360 cubic miles per day; total fuel consumption—24,000 tons per day. CPI = 67 tons fuel per cubic mile

anyone reading the reports cannot help but feel that he is contemplating the wreckage without having many clues as to the cause. We know that the great majority of the dead were respiratory or cardiac cripples. Evidence from postmortem material is virtually valueless because of its paucity. No well defined clinical syndrome was recognized. Many people were found dead in bed. Routine air pollution studies consisted of measurements of smoke and sulfur dioxide and these pollutants reached high levels. The danger we face in interpreting these data is to forget that they might merely be of significance as indicators of atmospheric pollution in general. In ascribing the disaster to either of these substances (which are selected for routine measurement mainly because of the ease with which they are determined, their ability as an indication of general pollution, and their obvious unpleasant character) we run the risk of following a monstrous red herring."

Dependable model

As has been noted, any of the well-known pollutants can be used to some

extent as an indicator of total air pollution if enough is known about the sources of pollution, meteorological conditions, and so on—in other words, if a sufficiently dependable model is available. It would be helpful, however, if it were possible to measure a single pollutant that would be reasonably proportional to the overall CPI. CO is primarily produced by automobiles, and to a much smaller extent, relatively speaking, by other forms of combustion. SO₂, on the other hand, is primarily produced in power plants and heating systems that use high-sulfur coal or oil. Both are known to cause physiological damage if present in high enough concentrations, so they must be monitored in any case. CO₂ is more nearly independent of the type of fuel and combustion process, since a large part of the mass of all commercial fuels is carbon and when burned in any reasonably efficient manner, most of the carbon is converted to CO₂. However, it is also produced by a number of natural processes and is, indeed, a normal and essential component of clean air. The average concentration in clean air is already 350 p.p.m. and the percentage change in concentration to be expected from

local combustion products does not make CO₂ concentration as sensitive an indicator as one would like.

Total CPI

Another possibility is the measurement of particles. Particles are produced by all forms of combustion, and the smaller particles, 10 microns diameter and smaller, remain in the atmosphere for a long time. Clean air has only a negligible number of particles, compared with that found under conditions of only moderate air pollution.

In the past, the total mass of the particles has been measured. The soiling effect of particles has been measured but this is a measure of the surface and blackness of the deposit which is difficult to interpret. Recent developments have made it practical to obtain continuous automatic recording of the particle concentrations (number of particles per cc.) and this is closely related to the combustion pollution index in a city. The conversion factor will vary with local conditions, running generally in the order of 3000 particles per square centimeter for one ton of fuel per cubic mile of air.

Particle formation

Particles are produced by the condensation of a solid or liquid product that exists originally as a vapor in the high temperature zone of combustion. The process can be visualized in an oversimplified way by the following steps: The vapor of the solid- or liquid-to-be cools below the boiling point. Supersaturation occurs. Small clusters of a few molecules appear due to random collisions and then the supersaturated portion of the vapor deposits on these embryos to form very large numbers of very small particles.

This can be a very rapid process when it starts—in the order of microseconds. The small particles have high thermal velocity and stick together when they collide, and the size gradually increases when time is allowed for the coagulation process to proceed.

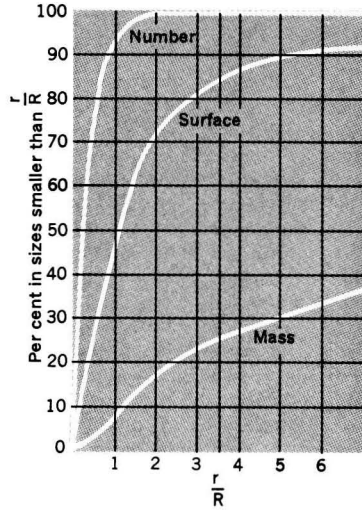


Figure 2. Typical aerosol size distribution:

r = radius of particle in cm.
 R = radius of particle of average mass in cm. (usually, about 5×10^{-6} cm).

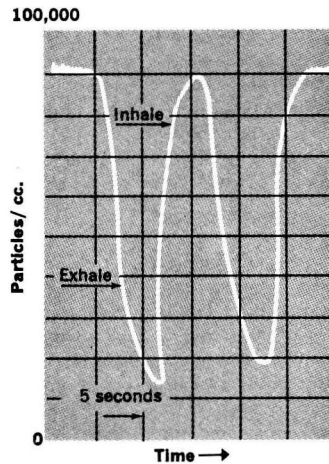


Figure 3. Condensation nuclei meter indication of particles per cc. in mouth during deep breathing through the mouth, showing about 80% retention of inhaled particles

At some point the mixture leaves the exhaust system and is rapidly diluted with the surrounding air, whereupon the coagulation process is slowed down drastically.

The number of particles produced per pound of fuel is relatively independent of the fuel. A dirty fuel produces bigger particles (not more particles) than a "clean" fuel burned under the same conditions. The number of particles is affected by the time of confinement in the exhaust system, but average values can easily be established. The number of particles of all sizes varies from a very low value over the open ocean to several million per cc. in metropolitan traffic.

Particle size

The size of particles making up a typical city aerosol ranges from approximately 0.01 micron in diameter to 100 microns in diameter. The smallest size is limited by the rapid coagulation of very small particles, both in the exhaust stack and in free air. The largest size is limited by the fall-out due to gravity. The combination of these two actions in time produces a similar size distribution in all natural aerosols. Some 98% of the number of particles, 75% of the surface, and some 18% of the mass in a typical aerosol is associated with submicroscopic sizes (see Fig. 2).

Physiologic effects

Not enough is known about the physiological effects of aerosol particles in the atmosphere to make a definite statement on the subject. Certain sizes of particles in this range are not efficiently filtered by nasal hairs or plated out on the walls of the

oral and bronchial passages and can, therefore, be carried deep into the lungs where they tend to deposit rather efficiently (see Fig. 3). There is reason to suspect, therefore, that at least some of the physiological damage attributed to air pollution may be caused by these microscopic and sub-microscopic particles, either as irritation-inducing agents in their own right, or as carriers of absorbed toxic gases. The relatively large surface area which they offer makes the latter idea especially interesting. Some research work is being done along these lines but it would appear that more is needed.

Particle measurement

Particles can be created in the atmosphere by the reaction of gases, notably in the case of photochemical smog. SO_2 in the air when exposed to sunlight changes slowly to SO_3 . The SO_3 picks up water to form sulfuric acid vapor. The vapor pressure of H_2SO_4 is low, so when enough SO_3 has been created to exceed this value, the excess condenses either on itself to form droplets of sulfuric acid or on other particles to coat them with a layer of sulfuric acid. More complicated reactions occur in nature, such as sunlight plus oxides of nitrogen producing ozone, which reacts with unburned hydrocarbons to produce a large number of gaseous liquid or solid compounds.

Thus, equipment used to measure particles can also be used to measure some types of gases. At the present stage of development, the specificity is not equal to advanced chemical methods, but there are conditions where this could be a virtue. If the air is filtered

to remove all particles and then passed over an ultraviolet light source any of several gases can produce particles. Normally SO_2 would predominate, but this system could pick up any gases that are convertible by u.v. In a similar fashion, the gases that react with an acid or base to produce condensable materials could be detected by passage over an acid or base. Such tests are based on accentuating some of the natural smog formation processes, and an abnormal concentration of a certain class of gas under smog conditions would be most suggestive. By a time-sharing scheme a single instrument to read particles, equipped with very simple accessories, could also collect data on gases of this nature. This technique has been used to measure gaseous pollutants in the laboratory, on naval vessels, and in industrial conditions.

Pollution control

Many vital aspects of pollution measurement and control have not been considered in this discussion. Local conditions may call for different degrees of emphasis and there can be justified variations from place to place. The purpose here is not to outline a rigid master plan but to suggest that:

- A measurement of the particle population will supply a useful index of pollution due to combustion.
- Particles by themselves or in synergistic situations are a factor in air pollution.
- Such measurements together with the more common measurement and proper modeling techniques can evolve into a system that will supply the kind of information required by pollution control authorities.

T. A. Rich is senior engineer, General Electric Research and Development Center. He received his B.S. (1930) in electrical engineering from Harvard University. Mr. Rich is a consultant, professional engineer, inventor, and recipient of numerous awards in the instrumentation field. He has been associated with the General Electric Company since 1923 and its R&D Center since 1932. For his development of the condensation nuclei counter and his work with methods for measuring size and electrical charge of small at-

mospheric particles he received international recognition in the field of atmospheric physics. On three separate occasions he was honored by G.E. with the Charles A. Coffin Award, its highest award for technical recognition. He is recipient of the 1960 Leeds Award of the American Institute of Electrical Engineers. Mr. Rich is a member of the Institute of Electrical and Electronics Engineers, Instrument Society of America, American Association of Contamination Control, American Meteorological Society, and ASTM.



Response of Single Particle Optical Counters to Nonideal Particles

Kenneth T. Whitby and Richard A. Vomela¹

Mechanical Engineering Department, University of Minnesota, Minneapolis, Minn.

■ The response of the Royco PC 200, Southern Research Institute (SRI), and Bausch and Lomb (B and L) single particle counters to nonideal but monodispersed aerosols has been measured. Aerosols used were polystyrene latex, dioctylphthalate, India ink, and polystyrene. The indicated size of the absorbing India ink was $\frac{1}{2}$ to $\frac{1}{6}$ of the true size for all of the counters. The Royco and SRI counters, which accept light through only a small solid angle, indicated a considerable spread in size distribution for the India ink and polystyrene particles which had some surface roughness. The resolution on rough-surfaced aerosols was better for the B and L counter which accepts light through a much larger solid angle. Experiments were also performed which showed that high concentrations of subcountable-sized monodispersed DOP aerosols (e.g., 10^4 per cc. of 0.25 micron) generated a relatively monodispersed distribution of impulse pulses within the counting range.

Dating from World War II, a number of instruments utilizing the light scattered by single aerosol particles have been developed for aerosol sizing and counting. Among the early ones are those described by Gucker and coworkers (1947, 1949, 1954, 1955, 1956); O'Konski and associates (1955, 1958 a, b); and Fisher, Katy, *et al.* (1955).

In recent years, several counters have become available commercially leading to their general use in such applications as clean room monitoring, air pollution measurement, and laboratory aerosol measurement. These include the Aerosoloscope developed by the Armor Research Foundation of Chicago and described by Fisher, Katz, *et al.* (1955), the Royco instrument described by Zinky (1962), the Southern Research Institute counter described by Thomas, Bird, *et al.* (1960), the new Bausch and Lomb counter described by Randall and Keller (1965), and the new counter described by Sinclair (1967). The important optical specifications and theoretical response characteristics of these counters are given in Table I.

The principle of operation of all of these counters is the same. Aerosol particles flow in a narrow stream through a

small sensing zone where they are illuminated by an intense beam of white light. The light scattered at an angle by individual particles is sensed by a multiplier phototube, resulting in an electrical pulse having an amplitude which is a function of the optical characteristic and size of the particle, and the design of the optical system. If the instrument is to be used to measure aerosol particle-size distribution, the pulses must be amplified and classified into amplitude ranges by a pulse height analyzer and counter.

Because of the complexity of the scattering process and of the optical and electronic components required, it is necessary to calibrate these instruments against particles of known particle size and optical properties.

The various aerosols and methods of preparation that have been used by a number of investigators are shown in Table II. The most common calibrating aerosol has been prepared by atomizing dilute aqueous suspensions of monodispersed polystyrene latex (PSL) obtained from the Dow Chemical Co. These aerosols have generally been assumed to be ideal transparent spheres. Although calibration with the polystyrene aerosols is simple and straightforward, the maximum size available is only about 3 microns. At present 0.088, 0.126, 0.264, 0.365, 0.557, 0.796, and 1.305 polystyrene latex, and 1.90 and 2.68 polyvinyl toluene latex are available from the Bioproducts Department of the Dow Chemical Co., Midland, Mich.

Other investigators have used pollens and spores as a larger monodispersed aerosol. Some have also prepared relatively monodispersed suspensions of glass beads and carbonyl iron. Table II shows that most of the irregular aerosols that have been used have also been quite heterodispersed because of the difficulty of generating monodispersed but optically irregular or optically absorbing particles.

Hodkinson and Greenfield (1965) have computed the response characteristic of several aerosol counters including the Royco, SRI, and Bausch and Lomb for transparent spheres of various refractive indices and for smooth opaque spheres. Their calculations for the three counters are shown in Figure 1. They showed that the response curves of the SRI counter on polystyrene latex of refractive index $m = 1.6$ as measured by Thomas, Bird, *et al.* (1960) and for the Royco, have the same shape as that computed from Figure 1, A and 1, B, respectively.

At the beginning of this study in 1963, there was little published data on the response characteristics of single

¹ Present Address, Environmental Research Corp., 3760 North Dunlap St., St. Paul, Minn. 55112

Table I. Characteristics of Commercially Available Automatic Particle Counters

Counter	Optical Specification				Size Range, Micron	Sampling Rate, CC. ³ /min.
	ψ	γ	β	η		
Royco PC 200	90	23.75	23.75		0.3-10	0.300 ^a
SRI	45	13.75	13.75		0.5-8	20
B and L		13.75	53.75	23.75	0.3-10	78
ARF Aerosoloscope	90				1-64	1800
Sinclair Phoenix		$\alpha = 11.25$	8.75	$\epsilon = 18.75$	0.3-16	2800

ψ = inclination of illuminating and collecting cone axis
 γ = semiangle of illuminating cone
 β = semiangle of collecting cone
 η = light trap semiangle
 α = illuminating cone—inside
 ϵ = illuminating cone—outside

^a Royco counter operated at sampling rate of 100 cc. per minute for all runs reported in Table III except 4 and 5.

Table II. Calibrating Methods Used by Various Investigators

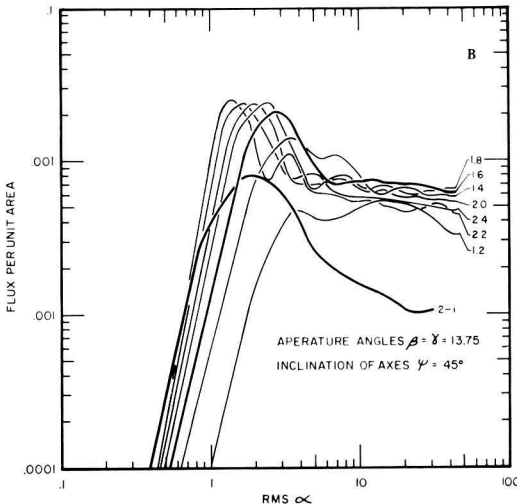
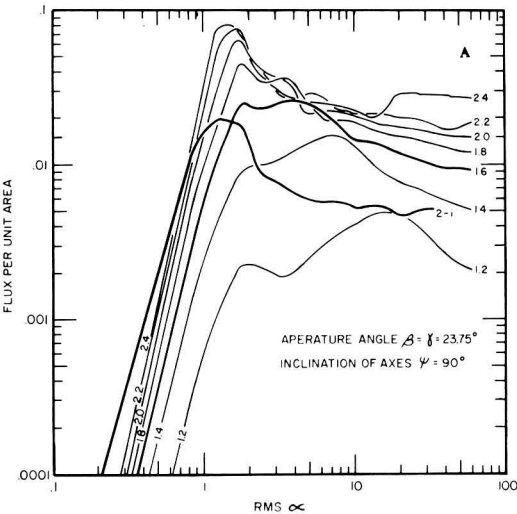
Reference	Material	Shape	Surface	Ref. Index	Aerosol Distribution		Preparation
					Mean Sizes	Spread	
O'Konski and Doyle (1955)	PS latex	Sphere	Smooth	1.6	0.132, 0.333, 0.514	2.1% < σ < 6.8%	Atomizer—no stabilizer
	Poly(vinyltoluene) latex	Sphere	Smooth		0.144, 0.470, 0.986	1.1% < σ < 2.8%	
Fisher, Katz, <i>et al.</i> (1955)	DOP	Sphere	Smooth	1.49	0.8-2		LaMer
	Spores	Sphere	?		2.5-25, 30-35		Air jet
	Glass beads	Sphere	Smooth		5-25		Air jet
	Carbonyl iron	Sphere	Smooth		0-7		Air jet
	Dibutyl phthalate	Sphere	Smooth		0.6, 20-35, 0-50		LaMer, spinning disk, air jet
Thomas, Bird, <i>et al.</i> (1961)	PS latex	Sphere	Smooth	1.6	0.27 to 3.2	Monodispersed	Atomizer
Eldridge (1961)	Glass	Sphere	Smooth	1.53	0-65	Heterogeneous	Air classifier
				1.9	0-40	Heterogeneous	Air classifier
				2.25	0-15	Heterogeneous	Air classifier
				2.5	0-15	Heterogeneous	Air classifier
Royco Instructions (1961)	PS latex	Sphere	Smooth	1.6	0.32-2.85	Monodispersed	Atomizer
	Special dust	?	?		1.05	$\sigma = 2.26$ micron	Air dispersed
	Iron oxide	Sphere	Smooth		2.8	$\sigma = 0.07$ micron	Air dispersed
	Puff ball spores	Sphere	Smooth		4.1	$\sigma = 0.035$ micron	Air dispersed
	Carbonyl iron	Sphere	Smooth		7.9	$\sigma = 8.8$ microns	Air dispersed
Zinky (1962)	PS latex	Sphere	Smooth	1.6		Monodispersed	Royco atomizer
Channell and Hanna (1963)	PS latex	Sphere	Smooth	1.6	0.156 to 3.04		Atomizer
	Silica flour	Irregular	Rough		1.6	Heterogeneous	Air dispersed
	Cement	Irregular	Rough			Heterogeneous	Air dispersed
	Diatomaceous earth	Irregular	Rough			Heterogeneous	Air dispersed
	Iron dust	Irregular	Rough			Heterogeneous	Air dispersed
	Coal dust	Irregular	Rough			Heterogeneous	Air dispersed
	Proposed ASTM Tentative, F-1 (1964)	PS latex	Sphere	Smooth	1.6	Available sizes	Monodispersed

particle counters on absorbing or irregular monodispersed aerosols. Therefore, the principal objective of the work reported here was to measure the response of these instruments to such aerosols. For comparison, the response to dioctylphthalate (DOP) droplets and to polystyrene latex (PSL) aerosols was also measured.

Experimental Apparatus and Procedures

Particle Counters. Three automatic optical counters have been evaluated to date. A brief description of each follows.

The Royco PC 200 is a highly automated counter capable of counting and sizing in 15 channels between 0.3 and 10 microns. Scattered light is received at essentially a 90° angle. The important optical parameters are shown in Figure 1, A. Our instrument is equipped with a Hewlett-Packard Model 560A digital printer.



When the instrument was received, it was checked carefully for proper operation and its calibration was checked using 0.814- and 1.17-micron PSL aerosols generated with the apparatus shown in Figure 2. These data (Runs 1 and 2, Table III) showed that the indicated size was equal to the known size of the PSL within experimental errors.

The instrument was then operated with no other adjustments than field calibration for the first year, after which it was returned to the factory for overhaul. Two other prime calibrations using the 0.814- and 1.17-micron PSL were made during the first year in addition to one at the end of the year (Runs 20-22, 40-43, and 67-68). The latter indicated a barely significant change in prime calibration. After the overhaul, the instrument was again calibrated with PSL (Runs 150-156).

The only maintenance required during the first year was

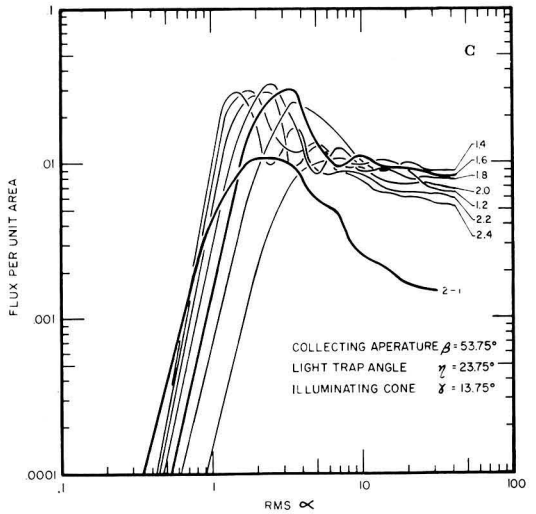


Figure 1. Scattered flux per unit area for the counters as a function of refractive index. The (2-i) curve is for adsorbing spheres after Hodkinson and Greenfield (1965)

- A. Royco counter
- B. Southern Research Institute counter
- C. Bausch and Lomb counter

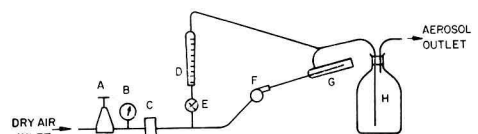


Figure 2. Generator for preparing aerosols from monodispersed hydrosols

- A. 0-30 p.s.i.g. regulator. B. Gage. C. Ultra filter. D. Flowmeter.
- E. Valve. F. Vaponefrin atomizer. G. Standard midget impinger with jet cut off 3 cm. from bottom. H. 1-Gallon bottle.

the repair of a decade counter. Zero air flow counts in all channels remained at zero.

The SRI counter, Figure 3, consists of an optical head containing two identical optical and flow systems (only one was used in this study), one electronics section, four dual channel strip chart recorders, and a 6-volt d.c. power supply. Relative count is recorded continuously in eight ranges: 0.5 to 0.7, 0.7 to 1, 1 to 1.4, 1.4 to 2.0, 2 to 3, 3 to 5, 6 to 8, and 8+.

This instrument measures light scattered at 45°. Its optical specifications and response curves are given in Figure 1,B. Prime calibration using PSL (Runs 32-33) showed that the instrument's measurements were too small at 1.3 microns and too large at 0.814 micron. Since the mean of these two runs was not significantly different than 1, the instrument calibration was not adjusted.

The Bausch and Lomb prototype counter, Figure 4, was loaned to the authors for two weeks. Its important optical parameters and response characteristics are shown in Figure 1,C. This counter uses an optical system that accepts light in a

full 360° around the optical axis at angles from 23.75° to 53.75°.

Particle counts greater than the selected size are read from a rate meter. Seven ranges are provided: 0.3, 0.5, 1.0, 2.0, 3.0, 5.0, and 10.0. The sampling rate is 78 cc. per minute. The instrument is compact and simple to operate.

A prime calibration using PSL was made (Runs 40-43). However, after these runs were completed and the instrument had been returned, it was discovered that the demineralized water was high in residue. Therefore, Runs 40 and 41 probably are somewhat questionable. These smaller sizes are adversely affected by background count from water residue. The prime calibration was not adjusted, and only the field calibration was used. The field calibration was somewhat unstable owing to malfunctioning of a compensating circuit.

Aerosols. Since the principal objective of this study was to measure the response of the counters on monodispersed but optically absorbing and irregular transparent particles over a broad range of sizes, the spinning disk aerosol generator

Table III. Summary of Data

Run No.	Aerosol	Microscope		Royco			SRI			Bausch and Lomb			Remarks
		Nmd	σ_g	Nmd	σ_g	C/M	Nmd	σ_g	C/M	Nmd	σ_g	C/M	
1	PSL	1.17		1.15	1.10	0.98							
2	PSL	0.814		0.86	1.09	1.04							
3	PSL	0.365		0.31	1.32	0.85							
7	MB	1.9	1.08	0.89	1.52	0.47							
7	MB	1.9	1.08	0.74	1.43	0.39							
20	PS	1.07	1.12	0.93	1.26	0.87	1.23	1.25	1.15				
21	PS	2.47	1.08	1.68	1.60	0.68	1.54	1.71	0.62				Some hollow
22	PS	5.50	1.07	4.8	1.87	0.87	1.54	2.91	0.28				
23	India ink	1.30	1.19	0.55	1.32	0.42	1.08	1.53	0.83				Spherical
24	India ink	2.50	1.09	0.44	1.32	0.18	0.74	1.46	0.29				Spherical
25	India ink	4.70	1.11	0.85	1.35	0.18	1.31	1.36	0.28				Spherical
26	India ink	10.2	1.19	1.93	1.92	0.19	1.87	1.72	0.18				
27	DOP			5.90	1.17		7.5	1.08					
29	DOP			1.35	1.27		1.60	1.32					
30	DOP			2.50	1.39		2.80	1.17					
32	PSL	1.30		1.27	1.26	0.98	1.20	1.15	0.92				
33	PSL	0.814		0.89	1.26	1.09	0.93	1.30	1.14				
37	DOP	5.60	1.04	5.45	1.09	0.97							
38	DOP	2.70	1.04	2.00	1.23	0.74							
40	PSL	0.365		0.40	1.82	1.11				1.15	1.48	3.2	
41	PSL	0.814		0.79	1.52	0.97				1.30	1.29	1.6	
42	PSL	1.17		1.17	1.52	1.00				1.33	1.19	1.14	
43	PSL	1.30		1.16	1.80	0.89				1.37	1.20	1.05	
46	DOP	1.90	1.18	1.84	1.25	0.97				3.1	1.15	1.62	
47	DOP	5.15	1.07	5.50	1.08	1.07				7.50	1.1	1.45	
49	India ink	1.17	1.14	0.47	1.30	0.40				0.64	1.83	0.55	
50	India ink	2.30	1.13	0.48	1.33	0.21				1.20	1.33	0.51	
52	India ink	4.50	1.12	0.99	1.36	0.220				1.60	1.15	0.36	
54	India ink	7.60	1.09	3.50	1.71	0.46				3.30	1.21	0.43	Irregular
55	PS	1.35	1.13	1.30	1.39	0.96				1.61	1.29	1.19	Some hollow
58	PS	5.10	1.07	7.30	1.43	1.43				7.50	1.1	1.47	
59	PS	1.87	1.11	1.67	1.56	0.89				3.50	1.1	1.87	
65	PSL	0.814		0.88	1.13	1.08							
67	PSL	1.17		1.26	1.16	1.08							
68	PSL	0.364		0.39	1.43	1.06							

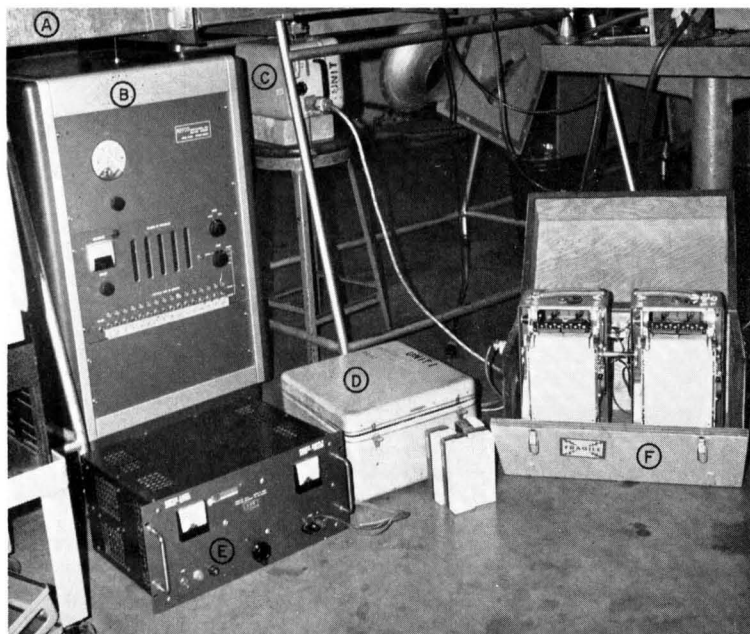


Figure 3. Royco and SRI counters

- A. Wind tunnel from which aerosol is sampled
- B. Royco counter
- C. SRI counter head containing optics and sampling system
- D. SRI electronics unit
- E. SRI power supply
- F. Two of four dual channel recorders

described by Whitby, Lundgren, *et al.* (1965) was selected to generate aerosols for this study.

Initially, India ink and polystyrene were selected as representative of completely opaque and ideal transparent particles, respectively. However, it was soon discovered that although the spinning disk generated polystyrene aerosols which were very nearly spherical, the particles had surface dents which significantly affected their optical behavior. Therefore, a procedure was developed for producing and sizing monodispersed dioctylphthalate (DOP) aerosols generated with the spinning disk since presumably the DOP droplets would be ideal transparent spheres.

Solutes and solvents used with the Model II spinning disk generator, described by Whitby, Lundgren, *et al.* (1965), to generate the various aerosols are given in Table IV. At the beginning of the project, some additional work on the satellite removal system was required to reduce the background aerosol to a few per cent of the count from the primary particles. All plastic and rubber tubing was eliminated from the liquid feed system to obtain dry polystyrene aerosols.

Representative photomicrographs of the polystyrene

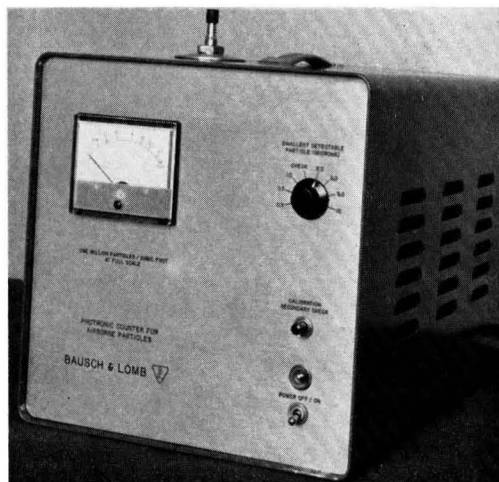


Figure 4. Bausch and Lomb counter

Table IV. Data on Aerosol Generation^a

Solvent	Solute	Solute Concentration, Wt. %	Approx. Particle Size Range, Microns	Particle Characteristics
Alcohol	Methylene blue	0.01-0.3	0.9-5	Spherical, dented, opaque
Alcohol	India ink	0.01-6	1 -10	Spherical, dented, opaque, rough surface
Xylene	Polystyrene	0.01-1	1 -5	Spherical, dented, transparent, smooth surface
Alcohol	Dioctal phthalate	0.01-6	1 -10	Spherical, transparent, smooth

^a Generated with Model II spinning disk at 45,000 r.p.m.

aerosols are shown in Figure 5. Figure 5,A shows that each particle has a dent. Some of the smaller PS aerosols had a few per cent of hollow particles (Table III). The electron photomicrograph, of approximately 1 micron PS (Figure 5,B), shows that the particles have smooth surfaces.

Figure 6 shows representative photomicrographs of India ink particles. These were generated by diluting ordinary India ink, having 12.5% solids, with ethyl alcohol to the solid contents given in Table IV. Figure 6,A shows an incident light microphoto of approximately 10-micron particles. These were the most irregular of the India ink particles generated. The smaller aerosols, such as those shown in Figure 6,B, were more nearly spherical in shape. The electron micrograph of Figure 6,C shows that the surface of these smaller particles is quite rough. This is because these particles are the residue of a suspension of submicron carbon particles rather than a true solution.

Figure 7 is a microphotograph of a typical DOP aerosol collected by an impactor on an oilphobic slide. Standard, clean microscope slides are made oilphobic by immersion for 5 minutes in a 0.2% solution of No. L-1083 fluorocarbon surfactant available from the Commercial Chemical Division of the Minnesota Mining and Manufacturing Co.

The PSL aerosol was generated with the apparatus shown in Figure 2 using hydrosols which are sufficiently dilute so that few doublets or triplets were produced. Figure 8 shows a typical frequency size distribution of the residue particles from the atomization of demineralized water and a water suspension of PSL as measured by a new electrical particle counting system (EPC) (Whitby and Clark, 1966). Total particle concentration larger than 0.002 micron was 2×10 cc., and the number median size was approximately 0.007 micron for the runs shown in Figure 8. The concentration of the PSL

leaving the generator was about 25 cc. Thus, there are approximately 10^4 residue particles per PSL particle leaving the generator.

Because high concentrations of particles smaller than 0.3 micron can cause optical counters to give false counts within the counting range, a few experiments were performed in which varying concentrations of monodispersed (DOP droplets of 0.125 micron ($\sigma_g = 1.2$) and 0.268 micron ($\sigma_g = 1.17$) sizes were mixed with atomized PSL of 0.796 micron size in low concentrations to measure this effect quantitatively. Monodispersed DOP aerosols were generated with a condensation generator of novel design (Liu, Whitby, *et al.* 1966), and size and concentration measured with the EPC.

Aerosol Sampling and Size Measurement. The aerosols generated by the spinning disk generator were introduced into the entrance of a 20-inch square wind tunnel (Whitby, Jordan, *et al.*, 1962) where they were diluted to a concentration of about 50 per cc. by mixing with particle-free air. The particle counters, mounted under the tunnel, Figure 3, sampled aerosol which passed through about 8 inches of small-diameter rigid tubing projecting 1 inch straight up into the tunnel. Tunnel velocity was 100 f.p.m. Experience with this system indicates that the sampling efficiency of the counters decreases for particles larger than about 5 microns, if sampling tubes longer than a foot or so are used. Accurate sampling of particles larger than 5 microns requires the use of short, rigid sampling tubes having large radii of curvature.

Solid aerosol samples for light microscopy were collected on 47-mm. diameter HA-type membrane filters using the direct flow isokinetic sampling system described by Whitby, Algren, *et al.* (1958). DOP droplets for microscopic size analysis were collected on oilphobic-coated microscope slides using a Unico cascade impactor. Solid aerosol samples for

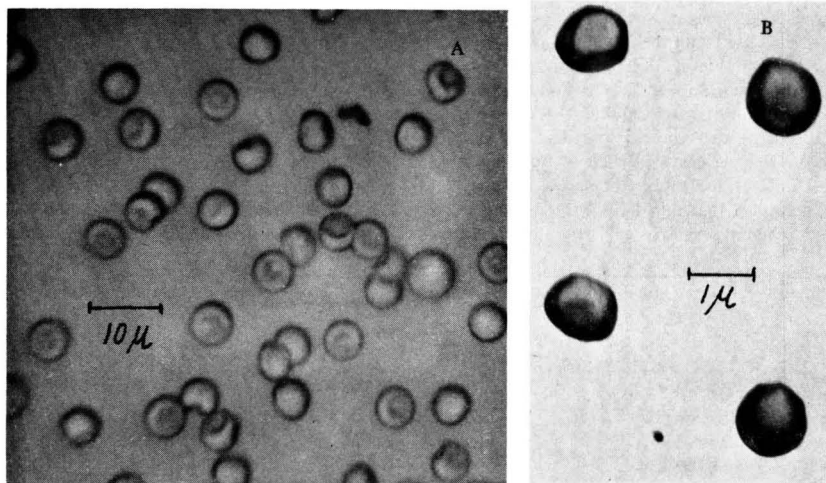


Figure 5. Spinning disk generated polystyrene aerosols

- A. Transmitted light
- B. Electron photomicrograph

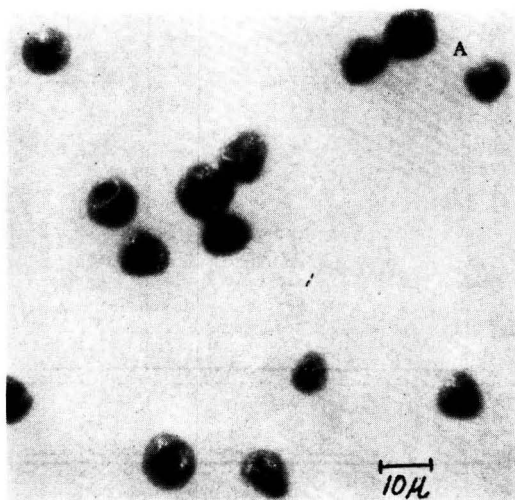


Figure 6. Spinning disk generated India ink particles

- A. Run 26
- B. Run 24
- C. Electron micrograph Run 49. Note surface roughness

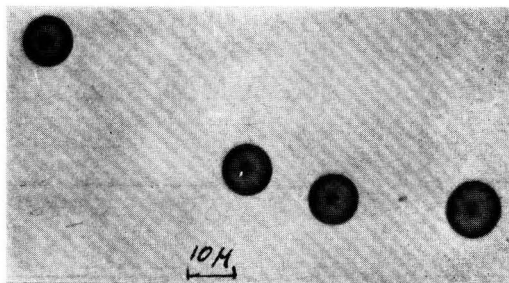


Figure 7. DOP droplets on oilphobic-treated microscope slide
Contact angle is 72° and true diameter is 0.66 times apparent diameter

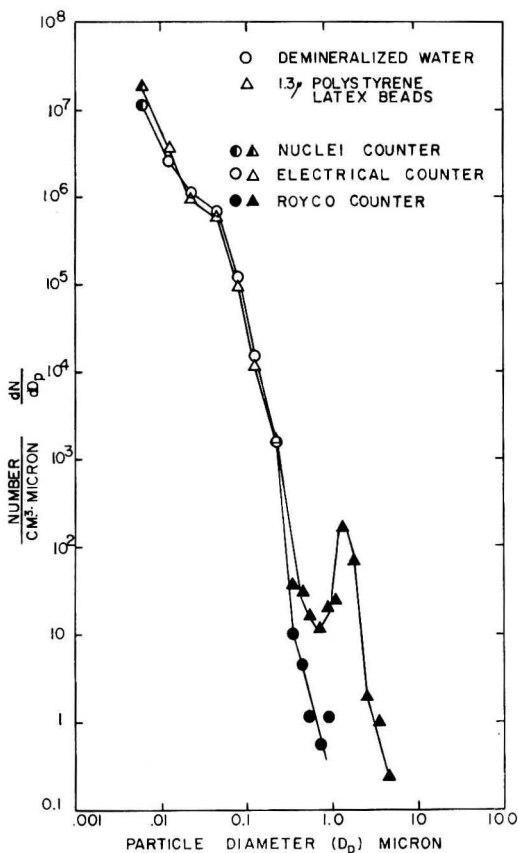
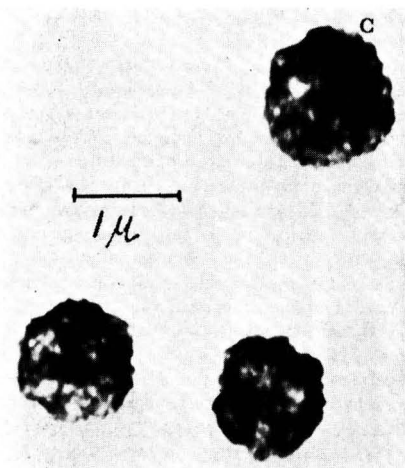
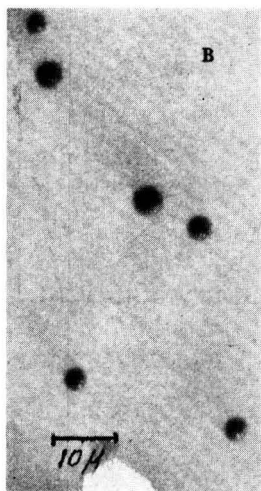


Figure 8. Size distribution of the residue from the atomization of demineralized water alone and a demineralized water suspension of 1.3 micron, PSL

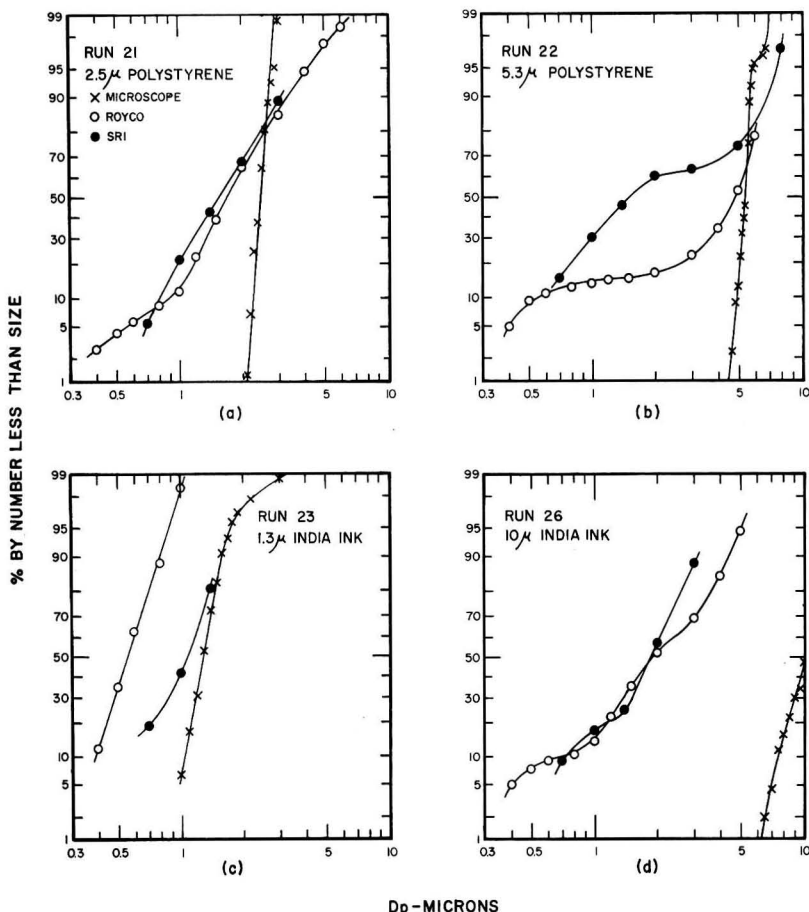


Figure 9. Typical cumulative plots of sizing data for the Royco and SRI counters

electron microscopy were sampled with a low pressure impactor directly onto Formvar-coated E.M. grids.

All aerosols larger than 1 micron were sized using a semi-automated Cooke AEI image-splitting eyepiece apparatus. Solid aerosols were sized directly on the membrane filter using a 100× oil immersion objective. DOP droplets were sized using a 45 × 0.6 N.A. dry objective. This apparatus is capable of accurate size analysis of nearly monodispersed aerosols. Estimated accuracy is about 5% for 5-micron particles, decreasing to about 20% for 1-micron particles.

Test Procedure. The particle counters were field calibrated and tested for zero background count on clean air before starting the aerosol generator. After the aerosol generator had been started and several Royco counting cycles had indicated that the aerosol concentration was stable, an aerosol sample was taken during the same period that the data from the counters were recorded. The Royco counter was operated at a sampling rate of 100 cc. per minute for all runs except 4 and 5.

Sufficient aerosol dilution was used for all runs so that the coincidence loss was negligible.

Conversion of Royco Indicated Size to Scattered Flux. To permit comparison of the measured scattered flux with the theoretical curve computed by Hodgkinson (Figure 13) one millisecond wide square, sinusoidal and triangular pulses were fed into the pulse height analyzer of the Royco, and the peak voltages required to just initiate counting in the channel above and to just stop counting in a channel were measured. The counting overlap between the channels measured in this way varied from 2 to 8% of the channel width.

The sinusoidal and triangular peak voltages required to just initiate counting in a channel were 7 and 16% higher, respectively, than for a square wave.

Assuming that the magnitude of the voltage pulse generated by the passage of a particle through the sensing volume is directly proportional to the light flux scattered by the particle, the relation between channel boundary particle size and pulse voltage may be used to convert the median aerosol particle

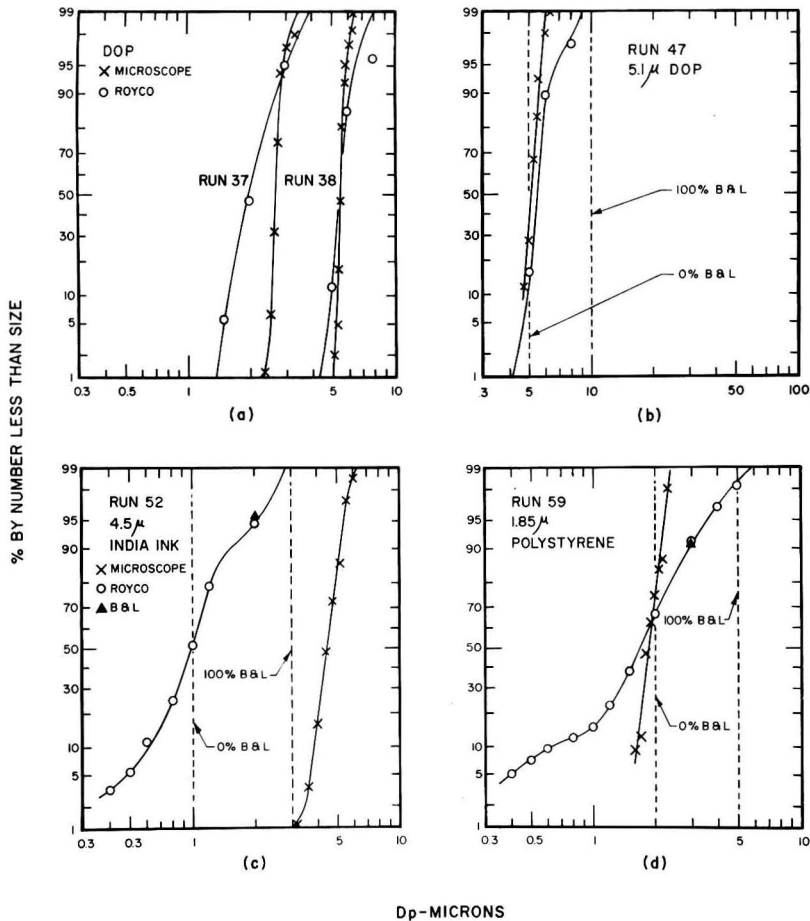


Figure 10. Typical cumulative plots of sizing data for the Royco and B and L counters

Dashed lines shown for the B and L counter indicate that all counts were above or below these size limits

size into relative flux in volts per square micron (Figure 13).

Royco Response to Particles with Diameters Less Than 0.3 Micron. Monodispersed DOP aerosols having sizes smaller than 0.3 micron were produced with the generator described by Liu, Whitby, *et al.* (1966). These were diluted with clean air and mixed with 0.79-micron PSL for Runs 157 to 163.

Results and Discussion

Data Reduction and Presentation. The size distribution data obtained from each counter and the corresponding microscope analysis of the aerosol were plotted as cumulative number-size distributions for all runs (Whitby and Vomela, 1965).

Typical cumulative size distributions calculated from the particle counter and microscope data are shown in Figures 9 and 10. Cumulative plots were used because the characteristic size can be much more accurately determined from the cumulative plot than can the mode from a frequency plot. This is especially true for the SRI and Bausch and Lomb counters which use rather broad class intervals for counting.

The number median diameters (nmd) tabulated in columns 5, 8, and 11 of Table III were read from the cumulative plots. The geometric standard deviations (σ_g) tabulated in columns 6, 9, and 12 of Table III were calculated by taking the square root of the ratio of the particle sizes at the 84 and 16% percentiles on the cumulative distributions.

With only a few exceptions, the cumulative distributions shown include the counts in all channels. For a few runs, the background and noise counts in the lower channels were neglected, but only if there was a clear minimum between the primary and background modes. Neglecting the counts in the lower channels has the effect of decreasing the σ_g slightly, but has a negligible effect on the nmd. Throughout all these experiments, size is reported in terms of the counter indication, the counter having been calibrated against PSL aerosol for the size ranges of about 1 micron.

Comparison of Indicated to Microscope Median Sizes. The ratio of the indicated to the microscope median sizes (C/M) for each counter is tabulated in columns 7, 10, and 13,

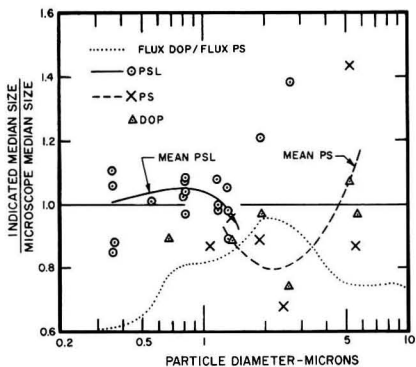


Figure 11. Comparison of indicated to microscope median particle diameters of polystyrene and DOP for the Royco counter

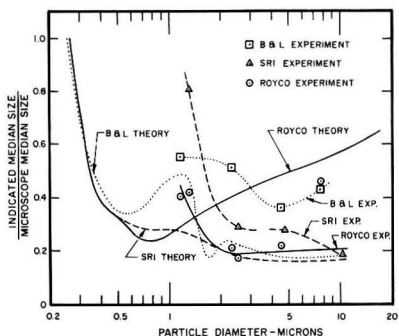


Figure 12. Comparison of indicated to microscope median particle diameter of India ink aerosols

Table III, for each run and also in graphical form in Figures 11 and 12. Several observations can be made from Figure 11 for the Royco counter:

The C/M for PSL is approximately 1 as would be expected. However, the C/M for the PS and DOP generated with the spinning disk appears to decrease to less than 0.8 between 2 and 3 microns before increasing to a value greater than 1 to 5 microns. Also, the C/M ratio for PS appears more variable than for DOP especially for the sizes near 5 microns. For example, the C/M for Run 22 (5.5 microns) is 0.87 and for Run 58 (5.1 microns) is 1.43.

The dotted line in Figure 11 was computed by taking the ratio of the flux for an index of refraction of 1.5 to that for 1.6 from Figure 1. Since the counters were calibrated using PSL having an index of refraction of 1.6, the C/M ratios for DOP Runs 46, 38, 37, and 47 would be expected to lie along the dotted line. However, the C/M's for DOP seem to be closer to

the mean PS line than to the theoretical DOP line. A similar examination of the data for the SRI and Bausch and Lomb counters reveals the following:

The C/M ratios for PSL and PS agree well and are equal to 1 at about 1 micron where they overlap for both the SRI and Bausch and Lomb counters. However, the C/M ratios for both counters are quite different from 1 for larger and smaller sizes, probably because the counters were only calibrated carefully by their builders near the 1.3-micron size.

The C/M ratio for PS and DOP is essentially the same for the Bausch and Lomb counter.

Several observations can also be made from Figure 12 which shows the C/M data obtained using India ink aerosols.

The theoretical C/M ratios for the SRI and Bausch and Lomb counters are essentially the same except for the peak at about 1 micron in the Bausch and Lomb curve. However, the theoretical C/M for the Royco increases from a minimum at about 0.8 micron.

Except for Run 54 on the Bausch and Lomb and Royco, the trend of the experimental C/M's decreases from 1 to 3 microns and then is relatively constant for larger sizes in a manner similar to the theoretical C/M curves for the SRI and Bausch and Lomb counters.

The Bausch and Lomb and Royco gave essentially the same C/M ratio (0.45) for the aerosol of Run 54, while the SRI and Royco gave the same C/M ratio (0.19) for Run 26. The data obtained during these runs were checked carefully, and the aerosols were studied microscopically with a Leitz Ultrapak to see if there were any significant differences. No errors were discovered, and no obvious differences between the aerosols were observed.

This suggests that the C/M ratio for all of the counters is very sensitive to small differences in shape and/or surface characteristics for opaque aerosols 4 microns and larger. Figure 6 shows that these aerosols are somewhat irregular, and that many of them have a prominent surface dent. Possibly, these irregularities dominate the scattering characteristics sufficiently so that the theoretical differences in the response of the counters are not observed.

However, it is not unreasonable to expect considerable sensitivity of the C/M ratios to particle shape and surface characteristics for large particles because most of the light is scattered at angles very close to the forward direction. Surface characteristics combined with particle irregularities could, therefore, cause large increases in the flux scattered at the acceptance angles of the counters. This may also be the reason for the large variation of C/M for the 5-micron PS aerosols.

Counter Resolution. An important characteristic of a particle counter is its ability to resolve an essentially monodispersed size distribution. This characteristic of the counters was measured by computing the geometric standard deviations (σ_g 's) from the counter data on each aerosol. The σ_g 's for each run are tabulated in columns 6, 9, and 12 of Table III and are summarized for each counter and aerosol in Table V.

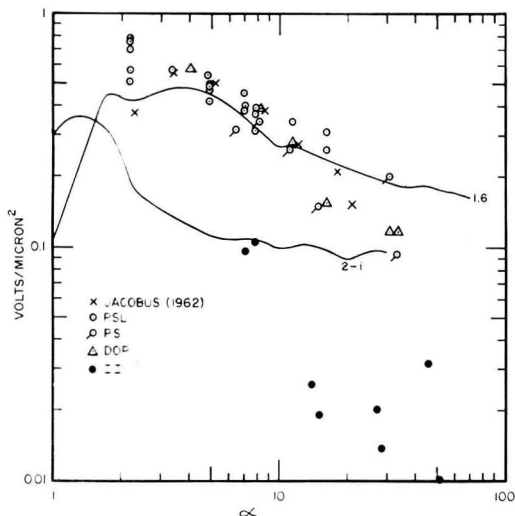


Figure 13. Relative flux per square micron expressed as volts/sq. micron on the different aerosols as measured with the Royco

and SRI optical systems which accept light in essentially only In Table V, the data have been grouped into four convenient size intervals for each aerosol.

A study of these data reveals the following:

The resolving power of all three counters on PSL in terms of the σ_g is essentially the same, decreasing from about 1.4 at 0.36 micron to between 1.15 and 1.2 at 1.3 microns. The decreasing resolving power for $D_p < 1$ micron may be due to the combined effects of instrument noise and the background count of submicron particles from the aerosol atomizer.

A contributing effect may also be due to the fact that the slope of the flux vs. α curves (Figure 3) in the range of $3 < \alpha < 6$ is quite negative. This might have the effect of accentuating the effects of any particle irregularities and shape variations.

The resolving power of all three counters on the 1- to 5-micron DOP aerosols is good and essentially the same, decreasing from a σ_g of about 1.25 at 1 micron to $\sigma_g = 1.1$ at 5 microns. The latter figure is essentially equal to the σ_g of the aerosol by microscope analysis.

The resolving power of the three counters on the PS and India ink aerosols is not only quite different, but is quite variable. With the exception of the 1-micron India ink aerosol, the resolving power of the Bausch and Lomb counter is clearly superior on the irregular and absorbing aerosols. The σ_g 's for the Bausch and Lomb counter decrease from about 1.3 at 1 micron to 1.2 at 10 microns.

For the Royco and SRI counters, the σ_g 's for the PS aerosol increase from about 1.3 at 1 micron to 1.6 for the Royco and 2.9 for SRI at 5 microns.

Similarly, the σ_g 's for these two counters on India ink aerosols are between 1.3 and 1.5 for sizes from 1 to 5 microns and then increase to over 1.7 near 10 microns.

The considerably better resolving power of the Bausch and Lomb instrument is probably due to the fact that its optical system integrates the light flux through 360° around the optical axis. This minimizes the effect of surface irregularities which may scatter significantly greater light flux in some particular direction. Thus, the light flux accepted by Royco

Table V. Mean Values for Different Aerosols

Aerosol	Micro. Nmd	Royco		SRI, σ_g	B and L σ_g
		C/M	σ_g		
PSL ^a	0.365	0.96	1.37		
	0.814	1.07	1.16	1.30	
	1.17	1.03	1.13		
	1.3	0.98	1.26	1.15	
PS	1-1.5	0.92	1.33	1.25	1.29
	1.5-2.5		1.58	1.71	1.1
DOP	5-6	1.15	1.60	2.91	1.1
	1-1.5		1.26	1.32	
India ink	1.5-2.5		1.26	1.17	1.15
	5-6		1.11	1.09	1.1
	1-1.5		1.31	1.53	1.83
	1.5-2.5		1.33	1.46	1.33
	5-7		1.36	1.36	1.15
	7-11		1.82	1.72	1.21

^a Runs 40 to 43 not included.

one direction is likely to be affected much more by the orientation with which the particle enters the sensing volume.

The sharp increase in σ_g for the Royco and SRI counters with increasing particle size is probably caused by the fact that as the size increases, the angular width of the forward scattering lobe contributes less and less to the flux accepted by the optical system. Thus, properly oriented surface irregularities, such as the dents in the polystyrene and India ink particles, may sharply increase the received flux. Also, the 7- to 10-micron India ink particles were more irregular than the smaller ones.

The σ_g of the three counters on 1.2-micron India ink particles is in the inverse order to what it is for the larger sizes, with the Bausch and Lomb being the highest and the Royco being the lowest. This is the particle size at which the

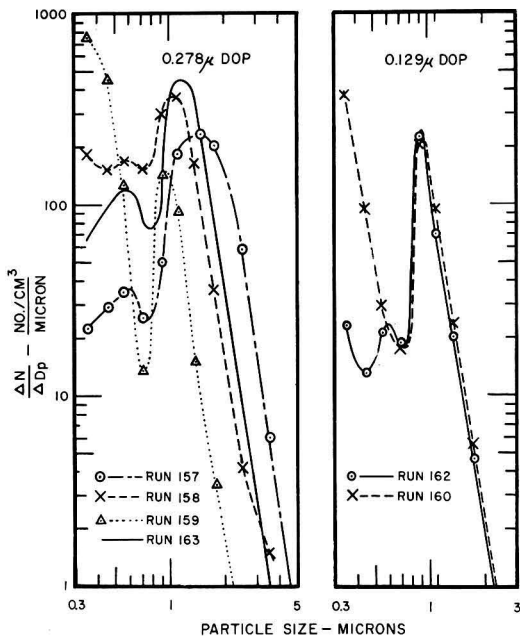


Figure 14. Indicated Royco size distributions produced when monodispersed DOP aerosols were mixed with the aerosol produced by atomizing 0.796 PSL in demineralized water

See Table VII for conditions for each run

Table VI. Comparison of Response Curve Slope and Resolving Power

Counter	Slope (2- <i>i</i>) for 5 < α < 10	σ_p - 1.25-micron India Ink
Royco	-0.16	1.31
SRI	-0.7	1.53
B and L	-1.1	1.83

σ_p 's of the counters on the transparent aerosols are essentially the same. This suggests that the observed difference for the India ink aerosols is connected with some difference in response characteristics of the three counters. An examination of the response curves of the three counters, Figure 1, shows that the negative slope of the flux vs. α curve, in the range $5 < \alpha < 10$, corresponding approximately to the particle size range $1 < D_p < 1.5$, is approximately proportional to σ_p , Table VI. This correlation might be explained on the basis that the greater the (-) slope the greater the relative effect of a small asphericity or surface inhomogeneity on the particle.

Comparison of the Experimental and Theoretical Flux. In Figure 13, the relative flux per square micron particle area for the Royco as computed by Hodkinson and Greenfield (1965), is compared with that computed from our data. The ordinate of the theoretical curve for $m = 1.6$ was located so that it went through the data for polystyrene at $\alpha = 6$. Both the PS and DOP data agree reasonably well with the curves from $\alpha = 3$ to $\alpha = 15$, but fall below the curve for $\alpha > 15$. The India ink aerosol for $\alpha = 8$ falls on the 2-*i* curve but falls far below for $\alpha > 10$.

Since it was not possible to measure the absolute flux scattered by the particles in these experiments, it is not known whether the differences for large α are due to nonlinearity between scattered flux and the pulse height or a real decrease in scattered flux. The DOP ($m = 1.49$) may be considered as an ideal smooth spherical aerosol, the PSL ($m = 1.6$) as a nearly spherical but slightly irregular aerosol. The flux from all three is essentially the same; therefore, the small difference in refractive index between polystyrene and DOP and the small surface dents of the polystyrene do not significantly affect the indicated median size of the essentially transparent spherical particles.

However, the flux scattered by the large India ink particles is almost one decade below the theoretical curve, indicating that the light scattered by these particles is substantially less than predicted. Evidently this is not caused by instrumental nonlinearity because the relative decrease in flux is so much more than that for the transparent particles. Possibly the irregular shape and rough surfaces of the India ink particles reduce the light scattered below that predicted.

Royco Response to Mixtures of PSL and DOP of Diameters Less Than 0.3 Micron. The results from the experiments in which 0.79-micron PSL atomized from a water suspension was mixed with varying concentrations of monodispersed DOP droplets are summarized in Table VII and Figure 13. A comparison of Run 162 (PSL and residue only) with Run 160 (PSL and residue plus 30,000 per cc. of 0.125-micron DOP), shows that the DOP causes sharply increased counts in the lower channels but an insignificant increase in the indicated size of the PSL. Run 159 (612 per cc. of 0.278-micron DOP plus PSL and residue) yielded results similar to Run 162. However, as the concentration of 0.278-micron DOP was increased, Runs 158 and 157, the counts in the lower channels

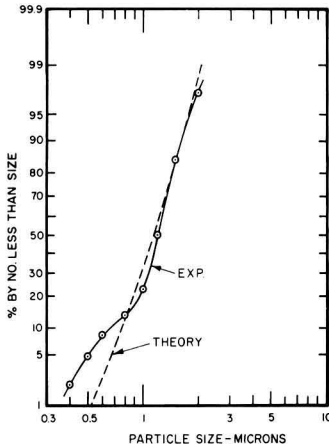


Figure 15. Comparison of theoretical and observed size distributions for Run 163

See Table VII for data

decreased and a significant increase in the indicated size of the PSL occurred. Since Run 163 with 40,700 per cc. of 0.278-micron DOP only also showed a mode at about 1.2 microns; apparently high concentrations of small aerosol particles can not only increase the indicated size of the PSL but can also cause indications that look very similar to that of a monodispersed aerosol of approximately the same size (Figure 14). Also, the count in the lower channels for Run 163 is low and of the same order of magnitude as that for Run 162 with PSL only.

In addition to the experiments described above, a run was made in which the optical system was filled with a high concentration of aerosol of $D_p < 0.3$, after which a filter was placed on the aerosol inlet. As the aerosol was gradually diluted and flushed from the optical system, the indicated distribution changed from that of a monodispersed aerosol of about 8 microns median size to a smaller and smaller size until it finally disappeared from the 0.3 to 0.4-micron channel.

The results of the experiments with high concentrations of aerosols of $D_p < 0.3$ may be summarized as follows:

High concentrations may be indicated as a quite monodispersed aerosol at any size within the counting range

depending on concentration. Counts in the lower channels may be very low.

Low and medium concentrations have a negligible effect on the indicated size of PSL, but high concentrations may increase the indicated size without giving a very high count in the lower channels—e.g., Run 157. However, low and medium concentration may show a high count in the lower channels—e.g., Runs 158 and 159.

Possibly the varying amounts and sizes of the residue particles generated by the PSL generators used by different investigators is the reason for the different σ_g 's observed. Counts have varied from 50 to 90% in the count channel.

A statistical theory for predicting the size distribution of spurious pulses generated by high concentrations of sub-micron particles has been developed and will be presented in a separate paper (Whitby and Liu, 1967). (See Figure 15.)

Miscellaneous Observations and Recent Studies. Since completing the above studies in June 1965, some additional work has been done. Although most of this will be reported in subsequent publications, some results are worth brief mention at this time.

Preining (1966) conducted experiments in this laboratory to measure the cross channel sensitivity of the Royco PC 200 quantitatively. Using monodispersed DOP aerosols in the size range from 0.3 to 1.2 microns, he found that the σ_g with which the Royco would indicate a perfectly monodispersed aerosol varied from 1.14 at 0.3 micron to 1.07 at 1.14 microns.

Preliminary studies with an improved PSL generator consisting of a Collision atomizer and an impactor as described by Whitby, Lungren, *et al.* (1965), have shown that the background count due to residue particles can be reduced to negligible values so that from 90 to 95% of the counts can be obtained in the correct channel. For atomizing 0.795-micron and larger sizes PSL, the atomizer is used alone and for the 0.365- and 0.55-micron PSL, the 3-micron cutoff impactor is used in series.

Several years of operating experience with various optical counters suggests that a thorough factory overhaul once a year is advisable if the counters are to be used for aerosol sizing

Table VII. Effect of 0.129- and 0.278-Micron Monodispersed DOP Aerosols on the Royce Response to 0.796 PSL Aerosols

	Run No.						
	157	158	159	160	161	162	163
DOP size, micron	0.278	0.278	0.278	0.129	0.129	None	0.278
DOP concn., No./cm. ^{3a}	43,014	9,776	612	30,000	284	None	40,700
PSL concn., No./cm. ^{3b}	52	77	56	56	66	59	None
Total concn., No./cm. ³	67,960	73,633	27,608	63,338	33,180	41,546	40,700
Indicated concn., Royco	297	288	188	155	81	78	328
Residue concn., No./cm. ³	24,894	63,790	26,940	33,282	32,830	41,487	None

^a Calculated from EPC data taking difference between run with mixed DOP and PSL and PSL only for size ranges including size of DOP.

^b Calculated from Royco data from size ranges including PSL size.

and counting to accuracies better than 20%. If these instruments are well maintained and are given a prime calibration every few months over the entire size range for which they are to be used, then sizing accuracies of better than 10% may be obtained.

Conclusions

Optical counters calibrated with polystyrene latex aerosols do underestimate the size of absorbing aerosols, such as India ink, by factors of 2 to 5. The size underestimation is of the order of magnitude predicted by theory. There are significant differences between the SRI, Bausch and Lomb, and Royco counters, the Bausch and Lomb showing the least underestimation and the Royco the most for India ink particles in the 1- to 10-micron range.

The median indicated size seems to be relatively independent of particle shape for both transparent and absorbing particles for sizes less than 5 microns. For particles larger than 5 microns, the effect of particle shape and surface characteristics seems to become greater as evidenced by increased scatter of the data for both transparent and opaque particles.

The ability of the counters to resolve a narrow size distribution (as measured by σ_g) is a function of particle size and type of aerosol and is different for the three counters. For both opaque and transparent irregular particles larger than 2 microns, the resolution of the Bausch and Lomb counter is near the theoretical value, whereas the Royco and SRI counters respond to particle irregularity by spreading the indicated size. All three counters showed near theoretical resolution of the DOP aerosols larger than 1 micron. There are indications that the resolving power of all three counters on PSL aerosols decreases below 1 micron. However, this must be studied further since the atomizer-dispersed PSL aerosol is not completely satisfactory for evaluating resolving power because it is a solid and because of its inevitable background of solution residue particles.

The absolute calibration of the counters for transparent aerosols was good between 1 and 1.5 microns for all counters; good below 1 micron for the Royco and SRI; fair for the Royco and Bausch and Lomb above 1.5 microns; and poor for the SRI above 1.5 microns (Figures 12 and 14). This should not be taken too seriously since it is always possible to calibrate a given counter on a given aerosol so that it will indicate the correct size. However, the data reported here do show the necessity of calibrating optical counters over the complete indicated size range.

High concentrations of aerosols below the normal counting range of the counters may be indicated as a relatively mono-dispersed aerosol having a median size which is a function of concentration.

We suggest that it is these spurious pulses which cause much of the so-called lower channel noise observed during calibration of optical counters with polystyrene latex aerosols. Such aerosols contain from 10^3 to 10^4 submicron residue particles for every latex particle.

Acknowledgment

The Southern Research Institute (SRI) counter was obtained on loan from the Litton Applied Science Division, Minneapolis, through the courtesy of A. R. McFarland. The Bausch and Lomb (B & L) counter was loaned to us for two

weeks through the courtesy of J. M. Randall of the Electronics Research and Development division of Bausch and Lomb.

Nomenclature

- m = refractive index, dimensionless
- σ_g = geometric standard deviation, dimensionless
- σ = standard deviation, dimensionless
- nmd = number mean diameter, micron
- C/M = ratio of number mean diameter as measured by a counter to that measured by the microscope, dimensionless
- D_p = particle diameter, micron
- α = the group $\pi D_p/\lambda$, dimensionless
- λ = wave length of light, micron

Literature Cited

- "ASTM proposed Tentative Test Method for the Continuous Counting and Sizing of Airborne Particles in Dust-Controlled Areas by the Light Scattering Principle." ASTM F-1 Committee, Tax Group X-A, 1964.
- Channell, J. K., Hanna, R. J., *Arch. Environ. Health* **6**, 386-400 (1963).
- Eldridge, R. G., *J. Meteor.* **18**, 671-76 (1961).
- Fisher, M. A., Katz, S., Lieberman, A., Alexander, N. E., *Proc. Third Nat. Air Pollution Symp.*, Pasadena, Calif., April 18-20, 1955.
- Gucker, F. T., *Proc. Ind. Instr. Conf.*, Lafayette, Ind., pp. 284-312 (1956).
- Gucker, F. T., O'Konski, C. T., *J. Colloid Sci.* **4**, 541 (1949).
- Gucker, F. T., O'Konski, C. T., Pickard, H. B., Pitts, J. H., *J. Am. Chem. Soc.* **69**, 2422 (1947).
- Gucker, F. T., Rose, D. G., *J. Appl. Phys. Suppl.* **3**, 5138 (1954).
- Gucker, F. T., Rose, D. G., *Proc. Third Nat. Air Pollution Symp.*, 1955. Exec. Headquarters, 727 West 7th Street, Los Angeles 17, Calif.
- Hodkinson, J. R., Greenfield, J. R., *Appl. Opt.* **4**, 1463-74 (1965).
- Liu, B. Y. H., Whitby, K. T., Yu, H. S., *Rech. Atmospheriques*, Paris, France, No. 3, pp. 397-406 (1966).
- O'Konski, C. T., Bitron, M. D., Higuchi, W. I., *ASTM Spec. Tech. Publ.* **250**, pp. 2-28 (1958a).
- O'Konski, C. T., Bitron, M. D., Higuchi, W. I., *ASTM Spec. Tech. Publ.* No. 234 (1958b).
- O'Konski, C. T., Doyle, G. J., *Anal. Chem.* **27**, 694 (1955).
- Preining, Othman, I Physics Institute, Vienna, Austria, unpublished data, 1966.
- Randall, K. M., Keller, J. D., *Electro-Optical Aerosol Counter Instr. AIHA Conf.*, Houston, Tex., May 3-7, 1965.
- "Royco Operating and Service Manual, PC 200A Particle Counter," Royco Instruments, Inc., 440 Olive Street, Palo Alto, Calif., 1961.
- Sinclair, D. L., *Air Pollution Control Assoc.* **17**, 105-108 (1967).
- Thomas, A. C., Bird, A. N., Collins, R. H., Rice, P. C., *Instr. Soc. Am. Conf. Preprint*, No. 23-SF60, (1960).
- Whitby, K. T., Algren, A. B., Jordan, R. C., Annis, J. C., *HPAC J. Sect.* **30**, 171-178 (1958).
- Whitby, K. T., Clark, W. E., *Tellus* **XVIII**, 2, 1966.
- Whitby, K. T., Jordan, R. C., Algren, A. B., *ASHREA J.* **4**, 79-88 (1962).
- Whitby, K. T., Liu, B. Y. H., "Generation of Countable Pulses by High Concentration of Sub-countable Particles in the Sensing Volume of Optical Counters," to be published in *J. Colloid Sci.*, November 1967.
- Whitby, K. T., Lungren, D. A., Peterson, C. M., *Intern. J. Air Water Pollution* **9**, 263-77 (1965).
- Whitby, K. T., Vomela, R. A., *Progr. Rept. Mech. Engr. Dept.*, University of Minnesota, May 1965.
- Zinky, W. R. J., *Air Pollution Control Assn.* **12**, 578-83 (1962).

Received for review June 26, 1967. Accepted October 4, 1967. This research was supported by the Bureau of State Services, U. S. Public Health Service, Division of Air Pollution, Grant No. AP00283.

The Proximate Calculation of the Solubility of Gypsum in Natural Brines from 28° to 70° C.

A. V. Metler and A. G. Ostroff

Mobil Oil Corp., Field Research Laboratory, Dallas, Tex.

Formulas are derived for calculation of the solubility of calcium sulfate in various concentrations of sodium, magnesium, calcium, chloride, and sulfate ions in solution at 28°, 38°, 50°, and 70° C. Corrections are included to account for the effect of a wide concentration range of excess common ion (Ca⁺² or SO₄⁻²). Results are compared with a large number of solubility determinations in solutions of widely varying salt content. Examples demonstrating the use of these formulas are given.

Because of the interest in gypsum solubility for chemists, geologists, hydrologists, and engineers, many investigations have been made of gypsum solubility in solutions of one other salt by Cameron and Seidell (1901) and others, but only a few investigations in solutions of mixed salts. Sodium, magnesium, calcium, chloride, and sulfate ions predominantly represent the dissolved salt content in most subsurface natural waters (including sea water and its concentrates). Sodium, chloride, and magnesium ions as well as the common ions (Ca⁺² and SO₄⁻²) have their independent effects on the solubility of gypsum. Ions such as bicarbonate, strontium, and barium limit the amount of calcium or sulfate in the water but cannot be said to influence the solubility of calcium sulfate as a whole. The small variation of pH among brines does not appreciably affect calcium sulfate solubility.

An empirical method for calculation of the solubility of calcium sulfate in oilfield-type brines based on literature data available was described by Stiff and Davis (1952). They gave no experimental solubility data. In their method, numerical factors were calculated and used in an equation to calculate calcium sulfate solubility in the presence of excess calcium or sulfate ion, sodium ion, magnesium ion, and chloride ion. The product of these factors and including a temperature factor was averred to give calcium sulfate solubility in a specified brine at a given temperature. Experimental deviations from these predictions have been observed by those who have had occasion to use this method. For example, the solubility of calcium sulfate calculated for a solution containing 58.46 grams per liter NaCl, 4.8 grams per liter Mg⁺², and 5 grams per liter excess Ca⁺² by Stiff and Davis is 9.47 grams per liter, whereas by the authors' measurements, it is only 3.02 grams per liter, an error of 219%. Corresponding errors may be found in the calculated results as the NaCl and Mg⁺² concentrations increase. Sample comparisons in Table I show deviations ranging up to

745% of the measured value. Tate, Venable, and Nathan (1964) showed that the procedure of Stiff and Davis is inadequate for calculating the solubility of gypsum in oilfield brines or similar waters, because the effects of salinity and temperature are not independent and additive as Stiff and Davis assumed, but they did not offer data or an improved method of calculation. Calculation of calcium sulfate solubility by the Stiff and Davis procedure produces large errors where the magnesium concentration in the water is comparatively large and when large amounts of common ion (Ca⁺² or SO₄⁻²) are present. Data for limited concentration ranges has been published (Denman, 1961; Glater, Ssutu, *et al.*, 1967; Shaffer, 1967).

Described herein is a method of calculation of calcium sulfate solubility in natural brines which is based on actual and extensive experimental data and which recognizes the interdependence and influence of salinity, kind of salinity, and temperature on calcium sulfate solubility. The method described here overrides the inadequacies of the Debye-Hückel theory for

Table I. Comparison of Calculated and Measured Solubility Values for Calcium Sulfate (Grams per Liter of Solution) 28° C.

Excess Ca ⁺² Meq./Liter	Calcd. Solubilities Na ⁺ , Meq./Liter ^a			Measured Solubilities Na ⁺ , Meq./Liter ^b		
	0	1000	3000	0	1000	3000
Mg ⁺² Absent						
0	2.09	6.26	7.51	2.01	6.05	7.18
250	1.17	3.51	4.21	0.80	2.61	2.83
500	1.09	3.26	3.91	0.50	1.71	1.65
750	1.02	3.07	3.68	0.44	1.35	1.20
Mg ⁺² = 400 meq./liter						
0	5.64	16.9	20.3	5.68	7.26	7.39
250	3.16	9.47	11.4	2.19	3.02	2.92
500	2.93	8.79	10.6	1.42	1.95	1.68
750	2.76	8.28	9.9	1.20	1.48	1.26
Mg ⁺² = 500 meq./liter						
0	6.16	18.5	22.2	6.15	7.38	7.46
250	3.45	10.3	12.4	2.40	3.11	2.87
500	3.20	9.60	11.5	1.54	1.98	1.72
750	3.02	9.05	10.9	1.30	1.51	1.30

^a Stiff and Davis, 1952.

^b Ostroff and Metler, 1966.

the more concentrated solutions and is specifically designed for use by engineers who are involved with the handling of field brines and requires the minimum number of calculations and conversions.

Experimentally Measured Solubilities

Solubility of calcium sulfate in the system sodium chloride–magnesium chloride–calcium sulfate–water has been reported by Ostroff and Metler (1966). These measurements were made at temperatures of 28°, 38°, 50°, and 70° C. in solutions of sodium chloride and magnesium chloride designed to represent subsurface brines.

The experimental procedure used to measure calcium sulfate solubility as well as the data obtained are fully described elsewhere (Ostroff and Metler, 1966). Briefly, the technique consisted of stirring solid calcium sulfate dihydrate in contact with sodium chloride–magnesium chloride solutions until the solutions were saturated. Solutions were then filtered through a 0.45-micron filter, and both the solid and filtrates were collected. The calcium sulfate crystal modification was identified by x-ray analysis. The filtrate was analyzed using standard methods for calcium, magnesium, and chloride ions. Sodium ion was calculated from the amounts of magnesium ion (added as magnesium chloride) and chloride ion (added as both sodium and magnesium chlorides) present. Frequently, sulfate and sodium also were determined. In the case of the solutions reported here which did not contain chemically equivalent concentrations of calcium and sulfate, both calcium and sulfate were determined.

Some natural brines from deep (oil) wells were collected and saturated with calcium sulfate. Concentrations of calcium and sulfate varied, but all of them contained excess amounts of calcium ion. Analyses are shown in Table IV. The same saturation and analysis procedures were applied to these solutions as in the earlier work.

Expression of Ionic Concentration

Results of water analyses are reported in various units. Probably the most widely used units are milligrams of solute per liter of solution and parts of solute per million parts of solution in weight units. Since the volume of the solution changes with temperature, the milligrams-per-liter expression accurately describes the concentration of dissolved components at only a specified temperature, usually that of the laboratory at the time of the analysis, whereas parts-per-million units are not influenced by temperature changes which may alter the volume of solution. The method described here for calculating gypsum solubility in underground brines uses water analysis data expressed in weight (p.p.m.) units to permit direct comparison of solubilities at different temperatures. Results of the solubility calculation described here can be simply converted to milligrams-per-liter units.

Ionic concentrations expressed in milligrams per liter must

be converted to parts per million before results of the water analysis are used to calculate calcium sulfate solubility. (This caution extends back even to the analytical procedure used in sampling or aliquoting samples at the beginning of the analysis, and this information must be ascertained from the analyst before beginning the calculation procedure described herein. In reporting water analysis results, some analytical laboratories do not distinguish between parts per million and milligrams per liter.) Milligrams-per-liter units are converted to parts per million simply by dividing the concentration in milligrams-per-liter by the specific gravity of the brine. The specific gravity of a field brine (which contains principally sodium chloride) is accurately expressed by the equation

$$\text{Sp. gr.} = 1 + \frac{\text{total dissociated solids (mg/liter of soln.)} \times 0.695 \times 10^{-6}}{1} \quad (1a)$$

If analysis is expressed as p.p.m.,

$$\text{Sp. gr.} = \frac{1}{1 - 0.695 \times 10^{-6} \text{TDS (p.p.m.)}} \quad (1b)$$

If analysis is expressed as milligrams per 1000 grams of H₂O,

$$\text{Sp. gr.} = \frac{1 + 10^{-6} \text{TDS (mg./kg. H}_2\text{O)}}{1 + 0.305 \times 10^{-6} \text{TDS (mg./kg. H}_2\text{O)}} \quad (1c)$$

The importance of using the proper units can be illustrated using this example. Suppose a brine having a total dissolved solids content of 240,000 mg. per liter has a chloride concentration of 140,691 mg. per liter. On converting to units of parts per million, the chloride ion concentration is 121,810 p.p.m. This represents an appreciable difference (16%) in numerical values and is indicative of the error which can be incurred by indiscriminately using milligrams-per-liter units as parts-per-million units. The magnitude of the error, of course, depends on the total dissolved solids in the water.

Solubility Product

The significance of an approximate solubility product used herein is that it offers the only simple and convenient method of expressing the degree of calcium sulfate saturation of a solution or brine.

When molecular amounts of calcium and sulfate ions are not equal, it is convenient to determine if the solution is saturated by comparing the product of the calcium and sulfate ions with a calculated solubility product, *K*. If this product is different than *K*, the amount of over or undersaturation can be determined. Thus when

$$(\text{Ca}^{+2}) > (\text{SO}_4^{-2})$$

$$\text{let } (\text{Ca}^{+2}) - (\text{SO}_4^{-2}) = (\delta)$$

where (δ) represents excess Ca⁺² and concentrations are in moles per 1000 grams of brine.

Table II. Constants for Use in Calculating *K* at Various Temperatures

Cl ⁻ , P.P.M.	28° C.		38° C.		50° C.		70° C.	
	<i>C</i> × 10 ³	<i>M</i> × 10 ⁷	<i>C</i> × 10 ³	<i>M</i> × 10 ⁷	<i>C</i> × 10 ³	<i>M</i> × 10 ⁷	<i>C</i> × 10 ³	<i>M</i> × 10 ⁷
1,000	0.319	1.03	0.498	1.78	0.310	2.93	0.330	2.39
2,000	0.394	1.14	0.520	1.71	0.360	2.86	0.370	2.36
5,000	0.589	1.18	0.642	1.67	0.500	2.67	0.500	2.27
7,000	0.701	1.31	0.730	1.62	0.590	2.54	0.591	2.21
10,000	0.814	1.62	0.858	1.53	0.730	2.34	0.715	2.11
20,000	1.33	1.13	1.28	1.24	1.21	1.69	1.14	1.81
30,000	1.79	0.748	1.66	1.07	1.61	1.40	1.55	1.49
40,000	2.14	0.481	1.95	0.942	1.94	1.15	1.88	1.19
50,000	2.37	0.342	2.19	0.810	2.18	0.994	2.14	0.957
60,000	2.49	0.320	2.33	0.755	2.32	0.883	2.31	0.786
70,000	2.49	0.387	2.39	0.708	2.36	0.835	2.40	0.685
80,000	2.42	0.462	2.37	0.687	2.33	0.805	2.41	0.619
90,000	2.29	0.544	2.29	0.660	2.25	0.727	2.36	0.606
100,000	2.13	0.563	2.18	0.584	2.14	0.601	2.27	0.551
110,000	1.97	0.618	2.03	0.435	2.04	0.271	2.17	0.473
120,000	1.84	0.386	1.90	0.162	1.97	-0.226	2.09	0.281
130,000	1.78	0.484	1.78	-0.214	1.97	-0.997	2.05	-0.108
140,000	1.80	-0.549	1.72	-0.766	2.07	-0.214	2.09	-0.683

Example: When Cl⁻ = 50,000 p.p.m. at 28° C. and
Mg⁺² = 1000 p.p.m.

$$K = C + 1000 (M)$$

$$K = 2.37 \times 10^{-3} + 1000 (0.342 \times 10^{-7}) = 24.042 \times 10^{-4}$$

Table III. Comparison of Analytical and Calculated Solubility in Presence of Excess SO₄⁻², Results with Synthetic Solutions, Parts Per Million (Mg./Kg.) at 28° C.

	Cl ⁻	Mg ⁺²	Ca ⁺²	SO ₄ ⁻²	Excess SO ₄ ⁻²	CaSO ₄ , Anal.	CaSO ₄ , Calcd.
1	34516	4698	1965	4631	0	6675	6451
2	34516	4698	1941	4677	26	6593	6434
3	34513	4697	1890	4942	411	6420	6189
4	34517	4697	1706	5178	1089	5797	6132
5	34511	4696	1666	5465	1472	5659	5576
6	34486	4694	1427	6455	3034	4847	4817
7	34258	4670	867	12596	10518	2944	2738
8	34089	4647	603	23497	22050	2050	1747
9	65702	4493	2067	4943	0	7021	7009
10	65692	4492	2099	5208	176	7130	6893
11	65694	4492	2033	5297	424	6906	6733
12	65693	4492	1944	5536	875	6605	6448
13	65693	4493	1833	5812	1415	6230	6133
14	65694	4493	1479	6686	3140	5026	5248
15	66840	4621	848	12060	10028	2880	3131
16	66562	4602	621	21267	19779	2109	1941
17	95763	4340	1921	4711	0	6525	6726
18	95752	4339	1979	4894	151	6722	6610
19	95754	4339	1901	4956	400	6457	6449
20	95755	4338	1837	5183	781	6240	6209
21	95757	4339	1728	5423	1280	5872	5837
22	95747	4339	1481	6264	2713	5031	5127
23	95588	4332	896	11180	9035	3042	3001
24	95367	4322	568	16816	15454	1929	2047
25	121363	4177	1747	4164	0	5934	6084
26	121353	4176	1746	4325	140	5931	5989
27	121353	4176	1674	4431	418	5686	5809
28	121356	4176	1598	4634	853	5428	5540
29	121351	4175	1508	5013	1397	5126	5225
30	121329	4176	1279	5949	2881	4348	4460
31	121093	4167	695	11495	9917	2359	2458
32	120547	4149	417	21537	20538	1415	1293

$$(\text{Ca}^{+2})_{\text{CaSO}_4} + (\delta) = (\text{Ca}^{+2})$$

Where the dissolved calcium sulfate,

$$S = (\text{Ca}^{+2})_{\text{CaSO}_4} = (\text{SO}_4^{-2})$$

$$K = [(\text{Ca}^{+2})_{\text{CaSO}_4} + (\delta)] \cdot (\text{SO}_4^{-2}) = (\delta) S + S^2 \quad (2)$$

$$S = \sqrt{\frac{(\delta)^2}{4} + K} - \frac{(\delta)}{2} \quad (3)$$

Using Equation 3, solubility of calcium sulfate can be determined in a brine having an excess of either calcium or sulfate ion if values for the empirical solubility product, K , are known.

By measuring the solubility of gypsum in a series of sodium chloride–magnesium chloride brines which cover the composition range of most underground waters, solubility product values can be obtained which are a measure of calcium sulfate solubility in actual field brines. The solubility data of Ostroff and Metler have been converted to concentration units in parts per million by weight and K values calculated at fixed concentrations of magnesium and chloride. These fixed concentrations varied from 0 to 10,000 p.p.m. and then in steps of 10,000 p.p.m. to 140,000 p.p.m. chloride and from 250 p.p.m. to 4,000 p.p.m. magnesium. The solubility values at fixed chloride concentrations were then plotted against magnesium concentrations, and equations for the graphs at each temperature were determined by means of a least squares fit of the data. The curves were straight lines represented by the familiar Equation 4 where M is the slope, C the intercept, and Mg^{+2} the concentration of magnesium ion in the brine expressed as parts per million. Values for M and C are given in Table II for temperatures of 28°, 38°, 50°, and 70° C.

$$K = C + M(\text{Mg}^{+2}) \quad (4)$$

Using values for K calculated from Equation 4 and the constants in Table II, the solubility in water can be calculated using Equation 3. However, experience showed that for waters where only a slight excess of calcium or sulfate ion exists, Equation 4 gave acceptable calculated solubility product values. Where a large excess of one of these ions is present, the common ion effect is disproportionate, and Equation 4 does not give satisfactory results.

At great concentrations of either excess calcium ion or sulfate ion, other factors or attributes become more influential and the common ion effect is not the same for equal concentrations of calcium or sulfate ion. Hydration or dehydration of ions and other interionic influences contribute to this unequal effect and there is no accepted theory to predict its magnitude. Because the value of K increases nonlinearly at large excess ion concentrations, an empirical correction was sought to be used with Equation 4. Using experimental data for excess amounts of both calcium and sulfate ion, the deviations from theoretical or calculated K values were used to determine the magnitude of an empirical correction factor for Equation 4 for concentrations of up to 20,000 p.p.m. excess. In its simplest form, this factor is unity increased by (δ) used as in Equation 5.

$$[K_c = C + M(\text{Mg}^{+2})] [1 + (\delta)] \quad (5)$$

where K_c is the corrected solubility product and (δ) is excess of calcium or sulfate ion in moles per 1000 grams of brine. A calculation illustrating the application of Equations 3 and 4 to the analysis of a field brine is given later.

Evaluation of Method

The applicability of Equations 3 and 5 using K_c for K for calculating gypsum solubilities in brines was determined by comparison of calculated and measured solubilities. Table III shows the comparison between calculated and measured solubilities in laboratory-prepared solutions with excess sulfate ion. Comparison of measured and calculated values in actual field brines having excess calcium ion are shown in Table IV. These brines were equilibrated with solid calcium sulfate to ensure saturation.

Data shown in Tables III and IV are actual raw data not smoothed. The agreement between measured and calculated values is considered generally to be very good, leading to the conclusion that Equation 3 offers a valid and reliable method for calculating calcium sulfate solubility in field brines. Using this equation, it is possible to predict scaling tendencies and to make intelligent decisions regarding mixing of brines.

The term $\log(K_{IP}/K_c)$, (where K_{IP} is the product of the molar concentration of Ca^{+2} and SO_4^{-2} from the analysis and K_c is from Equation 5) is useful as a gypsum scaling index, since a negative value is obtained for brines which are unsaturated with calcium sulfate while brines containing an excess give positive values. Also, an approximate value of the degree of under- or oversaturation can be obtained from the expression $S(\sqrt{K_{IP}/K_c} - 1)$ where S is the calculated solubility (Equation 3).

Sample Calculation of Gypsum Solubility

For purposes of illustration, assume that the analysis of field brine shown in Table V is reported in milligrams-per-liter concentration units.

1. Divide mg./liter concentrations by the specific gravity to convert to p.p.m.

2. Convert sulfate and calcium concentrations into moles per 1000 grams of brine by dividing p.p.m. SO_4^{-2} by 96,064 and p.p.m. Ca^{+2} by 40,080.

3. Determine (δ) , the excess moles of SO_4^{-2} or Ca^{+2} . $(\delta) = \text{excess Ca}^{+2} = 0.0557 - 0.0116 = 0.0441$.

4. Calculate K_c using Equation 5 and Table II.

$$K_c = [C + M(\text{Mg}^{+2})] [1 + \delta] \quad (5)$$

At 28° C., interpolating for $\text{Cl}^- = 86,245$ p.p.m.

$$C = 2.37 \times 10^{-3}$$

$$M = 0.511 \times 10^{-7}$$

$$K_c = [2.37 \times 10^{-3} + (0.511 \times 10^{-7})(723)] [1 + 0.0441]$$

$$K_{c(28^\circ)} = 2.52 \times 10^{-3}$$

5. Calculate solubility of calcium sulfate at 28° C. using Equation 3.

Table IV. Comparison of Analytical and Calculated Solubility in Presence of Excess Ca⁺². Results with Natural Field Waters, Parts Per Million (Mg./Kg.) at 28° C.

	Cl ⁻	Mg ⁺²	SO ₄ ⁻²	Ca ⁺²	Excess Ca ⁺²	CaSO ₄ , Anal.	CaSO ₄ , Calcd.
1	1793	17	1842	806	38	2610	2595
2	6232	14	1989	1091	262	2818	3090
3	6414	13	2182	1026	116	3092	3335
4	15100	500	2588	1785	705	3667	3602
5	16759	223	3228	1654	308	4574	4224
6	33895	1065	2383	3666	2672	3377	3216
7	35880	653	3178	2695	1369	4504	4344
8	36162	746	3288	2553	1182	4660	4623
9	39708	914	2992	2771	1515	4241	4388
10	42158	1347	3248	2960	1600	4603	4408
11	42434	1334	3124	3090	1787	4428	4082
12	55362	1702	1974	5148	4324	2798	2903
13	57321	2535	1725	6399	5680	2444	2471
14	60814	2535	1418	8528	7937	2010	1974
15	70429	763	1652	6199	5510	2341	2503
16	72493	2896	1420	8060	7468	2012	2088
17	74878	2453	1460	7519	6910	2070	2192
18	78371	591	3112	3198	1900	4410	4403
19	85063	1173	1483	8637	8019	2101	1843
20	85460	2212	1298	8588	8046	1839	1883
21	85429	2302	1189	9537	9040	1695	1729
22	86308	1993	1408	7529	6941	1994	2042
23	90314	2336	1345	7908	7346	1906	1969
24	90388	90	1167	9509	9022	1654	1613
25	107289	8343	901	14667	14290	1277	1266
26	118495	3412	764	11138	10819	1083	1120
27	121414	5064	741	14682	14372	908	1034

$$S = \sqrt{\frac{(0.0441)^2}{4} + 2.52 \times 10^{-3}} - \frac{0.0441}{2}$$

= 0.0329 mole/1000 grams brine

(To convert moles/1000 grams brine to p.p.m. multiply by 136,144; mg./liter multiply by sp. gr. × 136,144; grams/liter multiply by sp. gr. × 136,144; moles/liter multiply by sp. gr.; lb./1000 bbl. multiply by sp. gr. × 136,144 × 0.35)

6. Calculate the actual amount of dissolved calcium sulfate present CaSO₄ (dissolved) = SO₄⁻² by analysis = 0.0116 mole/1000 grams brine.

7. To determine the actual amount of calcium sulfate this

brine will dissolve, solve the following equation for x, the additional moles of calcium sulfate that will be dissolved.

$$K_c = (\text{Ca}^{+2} + x)(\text{SO}_4^{-2} + x)$$

$$2.52 \times 10^{-3} = (0.0557 + x)(0.0116 + x)$$

$$x = 0.0208 \text{ mole CaSO}_4/1000 \text{ grams brine}$$

If brine was oversaturated (-x) should be used, and the concentration of calcium sulfate precipitated will be determined.

8. Calculate the relative measure of saturation. Since log(K_{IP}/K_c) is negative, this water is undersaturated with respect to calcium sulfate.

$$\log(K_{IP}/K_c) = \frac{(0.0557)(0.0116)}{2.52 \times 10^{-3}} = -0.592$$

Table V. Analysis of a Field Brine

	Mg./Liter	P.P.M.	Mole/1000 Grams Brine
CO ₃ ⁻²	0	0	
HCO ₃ ⁻	32	29	
SO ₄ ⁻²	1,239	1,120	0.0116
Cl ⁻	95,387	86,245	
Ca ⁺²	2,470	2,233	0.0557
Mg ⁺²	800	723	
Na ⁺	58,083	52,516	
Iron	6	6	
TDS	158,017		
pH	5.8		
Sp. gr.	1.106		

Literature Cited

Cameron, F. K., Seidell, A., *J. Phys. Chem.* **5**, 645-55 (1901).
 Denman, W. L., *Ind. Eng. Chem.* **53**, 817-22 (1961).
 Glater, J., Ssutu, L., McCutchan, J. W., *ENVIRON. SCI. TECHNOL.* **1**, 41-5 (1967).
 Ostroff, A. G., Metler, A. V., *J. Chem. Eng. Data* **11**, 346-50 (1966).
 Shaffer, L. H., *J. Chem. Eng. Data* **12**, 183-9 (1967).
 Stiff, H. A., Davis, L. E., *J. Petroleum Technol.* **4**(2), 25-8 (1952).
 Tate, J. F., Venable, R. L., Nathan, C. C., Division of Petroleum Chemistry, 148th Meeting, ACS, Chicago, Ill., August 1964.

Received for review June 7, 1967. Accepted September 25, 1967.

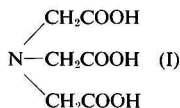
Biodegradation of Nitrilotriacetate in Activated Sludge

R. D. Swisher, M. M. Crutchfield, and D. W. Caldwell

Inorganic Chemicals Division, Monsanto Co., St. Louis, Mo. 63166

■ Nitrilotriacetate may become an important component in detergent formulations in the future, and thus may become a minor component of domestic sewage. However, no significant effects upon the general environment are to be anticipated, since laboratory studies show substantially complete biodegradation. Both fill-and-draw (24-hour cycle) and continuous-flow (6-hour and 3-hour retention) activated sludge units were used, fed synthetic sewage containing NTA at levels from 20 to 500 mg. per liter; the NTA-iron complex was degraded as well as free NTA. The added NTA caused no upsets in the normal functioning of the units. NTA can serve as the sole source of organic carbon for activated sludge, demonstrated by operation of a fill-and-draw unit for 6 months under such conditions. NTA analyses were by a non-specific method involving chelation of ferric iron.

Nitrilotriacetic acid (NTA) (I) contains three carboxyl groups and a basic nitrogen in a single rather small molecule. Strong chelating properties result; in aqueous solution the nitrilotriacetate ion combines stoichiometrically with polyvalent metal ions to give soluble complex ions of such stability that many of the characteristic chemical properties of the free metal ions are no longer exhibited.



Chelation of the calcium and magnesium ions present in hard water is one of the several functions performed by sodium tripolyphosphate (STP) in detergent formulations, and it has been found advantageous in some circumstances to replace a part of the STP by NTA. Complete replacement does not appear feasible, because some deterioration in performance then results. If use of NTA in detergent formulations became common commercially, the NTA would pass into sewage, and if not degraded therein, the average level might be on the order of several milligrams per liter. The present work was undertaken to gain some insight into its subsequent fate and the consequent environmental effects which might be anticipated. Meanwhile, Bunch and Ettinger (1967) have reported that NTA is biodegradable under the conditions of the Bunch-

Chambers (1967) test, a synthetic medium inoculated with sewage organisms.

The present results show that the activated sludge sewage treatment process readily degrades NTA, as evidenced by loss of its chelating properties. Furthermore, the most likely intermediate degradation products would be glycine and glycolic acid; these are not at all exotic, but instead should enter the natural biochemical processes with no difficulty because they are natural metabolic intermediates in living cells. If the first step of the degradation is hydrolytic, these two products should be formed directly. If, on the other hand, the first step is oxidative, they still might appear at a later stage in the fragmentation of the molecule.

These considerations suggest that no significant incremental effects are to be anticipated when such sewage enters our environment after normal sewage treatment. The degradability of NTA by the bacterial species which constitute activated sludge also suggests that even when raw sewage is released without treatment, NTA therein will be degraded in the receiving waters and soils via the same biochemical mechanisms, carried out by the naturally occurring bacteria which belong to these same species. Under such circumstances, small amounts of undegraded NTA might temporarily be present, but this should introduce no hazard beyond that of the raw sewage itself, because NTA is substantially nontoxic. Pollard (1966) has reported the absence of any effects by NTA on fish up to at least 100 mg. per liter, and on mammals fed orally, up to several thousand milligrams per kilogram.

Experimental Materials

NTA. Hampshire Chemical Division, W. R. Grace & Co., trisodium salt monohydrate, molecular weight 275, said to be about 99% pure. Although introduced into the biological systems in this form, throughout this report weights and concentrations are expressed in terms of the free acid, molecular weight 191. Thus, a 100 mg. per ml. stock solution would be made by dissolving 145.4 grams of the Hampshire product in water and diluting to 1 liter.

C₁₂ LAS (Linear Alkylbenzene Sulfonate). Soap & Detergent Association (SDA), 1-dodecene derived reference LAS No. 2, November 1964, 89.8% active. A mixture of 2-, 3-, 4-, 5-, and 6-phenyldodecane sodium sulfonates made by alkylation of benzene with 1-dodecene and sulfonation of the product.

Biodegradation Procedures

Semicontinuous Activated Sludge. The confirmatory test procedure of the SDA (1965) was followed, using activated

sludge obtained from a plant treating mostly domestic sewage. Briefly the SDA procedure calls for fill-and-draw operation using 1500 ml. of mixed liquor, suspended solids of about 2500 mg. per liter, 23-hour aeration, 1/2-hour settling, and 1/2 hour for withdrawing 1 liter of supernatant effluent and refilling with 1 liter of fresh feed. Standard feed was made from tap water by adding:

	Mg./Liter
Glucose	130
N broth ^a	130
Beef extract	130
K ₂ HPO ₄	130
(NH ₄) ₂ SO ₄	25
C ₁₂ LAS (active)	20

^a N broth consists of tryptone (a peptone) 20 grams, NaCl 5 grams, K₂HPO₄ 4 grams, KH₂PO₄ 1.5 grams, sodium desoxycholate 0.1 gram.

For operation with NTA as the sole organic carbon source the feed was:

	Mg./Liter
NTA	500
K ₂ HPO ₄	100
C ₁₂ LAS (active)	20

Continuous Activated Sludge. Fresh activated sludge from a plant treating mostly domestic sewage was maintained in the glass units (Figure 1) described previously (Swisher, O'Rourke, *et al.*, 1964). The working volume of the aeration section was 300 ml., of the settling section 75 ml., and air flow rate was about 100 ml. per minute. The synthetic sewage was made up from city tap water by adding:

	Mg./Liter
N broth	150
K ₂ HPO ₄	50
NaCl	30
MgSO ₄	10
C ₁₂ LAS (active)	20
NTA	0, 20, or 200
FeCl ₃	0 or 17

Feed was introduced at 50 or 100 ml. per hour, giving aerator residence times of 6 or 3 hours. Mixed liquor suspended solids levels remained at about 3000 to 4000 mg. per liter throughout the 3 months of operation. Each unit re-

ceived a daily inoculum of about 5 ml. of fresh sludge in order to maintain a diverse microbial population.

Chelometric Analysis for NTA

This analytical method is capable of determining NTA in activated sludge effluents in the concentration range 5 to 50 mg. per liter. It utilizes the formation of a stable, soluble, 1 to 1 complex between NTA and ferric ions. Excess ferric nitrate is added at pH 2; the uncomplexed iron is precipitated as hydrated ferric oxide under controlled conditions at pH 4 and is then removed by filtration. Soluble iron in the clear filtrate is then determined colorimetrically using a phenanthroline method, the total soluble iron being equivalent to the amount of NTA. Normal levels of metal ions do not interfere, nor do phosphates at typical concentrations. Other strong natural or synthetic chelating agents having ferric ion stability constants of 10¹³ or over can interfere.

Analytical results on known solutions of NTA are shown in Figure 2. In distilled water the amount of NTA found was in good agreement with the amount added. Statistical analysis indicates an uncertainty of about ±10% (95% confidence). Similar results were obtained in effluents from a semicontinuous activated sludge control unit fed no NTA, except for interference by natural chelating materials corresponding to about 4 to 5 mg. per liter of NTA. The natural chelants found in the effluents appear to be proportional to the amount of organic nutrient in the feed, since corresponding effluents from a continuous sludge control unit averaged only about 2 mg. per liter of apparent NTA. The feed to this unit aver-

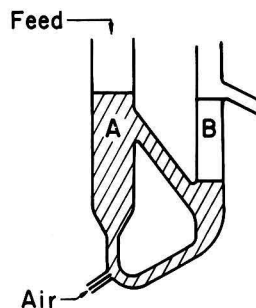


Figure 1. Continuous-flow activated sludge unit

A. Aerator, working volume 300 ml. (shaded section)

B. Settler, working volume 75 ml.

Table I. Apparent NTA in Continuous Flow Feeds

Days	Apparent NTA, Average, Mg./Liter		
	Fed 0 NTA	Fed 20 NTA	Fed 200 NTA
0-49	1.0 ± 0.5	17.6 ± 2.0	184 ± 16
50-63	0.7 ± 0.2	19.4 ± 0.5	195 ± 10
			Fed 20 NTA + Fe
64-77	0.8 ± 0.3	21.0 ± 1.0	24.7 ± 2.9

Table II. Apparent NTA in Continuous Flow Effluents

Residence,		Apparent NTA, Average, Mg./Liter		
Days	Hr.	Fed 0 NTA	Fed 20 NTA	Fed 200 NTA
16-49	6	1.8 ± 0.3	1.6 ± 0.3 ^a	8.7 ± 4.6 ^b
50-63	3	1.6 ± 0.2	1.4 ± 0.2	13.1 ± 2.3
				Fed 20 NTA + Fe
64-77	6	2.0 ± 0.4	1.9 ± 0.2	2.0 ± 0.3

^a Day 23 omitted. ^b Day 16 omitted.

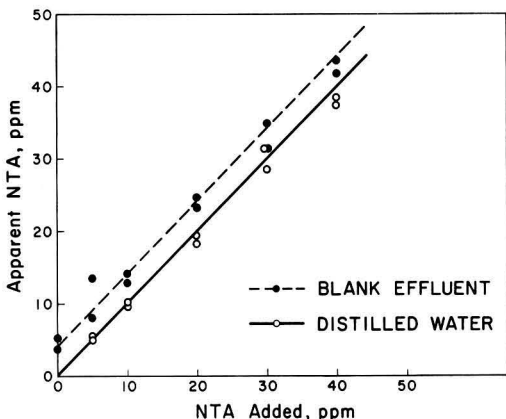


Figure 2. Calibration curves for chelometric NTA analysis

aged less than 1 mg. per liter of apparent NTA (Tables I and II).

Special Equipment and Reagents. Millipore filters (100- μ , 47-mm. diameter) and filtration apparatus. Spectrophotometer.

Ferric nitrate solution. Dissolve 2.20 grams of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 1 liter of water. Five milliliters of this solution is equivalent to 5.2 mg. of NTA.

Ammonium hydroxide-nitrate solution. Dissolve 35 ml. of 3M NH_4OH and 8 grams of NH_4NO_3 to make 1 liter of aqueous solution, approximately 0.1M in each.

Phenanthroline reagent. FerroVer powder pillows, No. 854 (Catalog No. 9, page 25), Hach Chemical Co., Ames, Iowa.

Analytical Procedure. A 100-ml. sample containing no more than 5 mg. of NTA—i.e., 50 mg. per liter of NTA;

stronger samples should be prediluted—is placed in a 400-ml. beaker and adjusted to pH 2.0 to 2.5 with concentrated HCl (1 to 2 drops are required). Add 5.0 ml. of ferric nitrate solution, heat to boiling with constant stirring, and add ammonium hydroxide-nitrate solution from a buret (about 0.1 ml. per second) until a pH of 3.9 to 4.1 is reached (5 to 10 ml. are required; pH meter should be set for 100° C.). The solution is boiled with stirring for another 5 minutes, a few drops more of ammonium hydroxide-nitrate being added if necessary to maintain pH 4. The volume of the solution should be less than 100 ml. at this time. It is cooled to room temperature, Millipore filtered by suction. To avoid peptization the precipitate is not washed. The filtrate is made up to 100 ml. with distilled water.

For the iron determination a 25-ml. sample of the filtrate is shaken with the contents of a FerroVer powder pillow in a 4-ounce bottle to dissolve, and within 2 to 9 minutes the absorbance of the solution is measured at 505 $m\mu$ —e.g., using a Spectronic 20 instrument with $\frac{1}{2}$ -inch cell. Reference to a calibration curve, made using known concentrations of ferric nitrate in water, gives the iron content in milligrams per liter, and the NTA content, which is 3.42 times the iron content.

Biodegradation Results

Effects of NTA on Sludge Process. The functioning of the laboratory activated sludge units was checked as described below by examination of LAS removal, chemical oxygen demand (COD) removal, sludge synthesis, and sludge settling. Effects were negligible for the most part, even at NTA levels up to 200 mg. per liter. There was no indication that any difficulties in sewage treatment plant operation might result from the very low concentrations which might be met in the field.

All feeds contained 20 mg. per liter of C_{12} LAS in addition to the organic nutrients, and the effluents were monitored

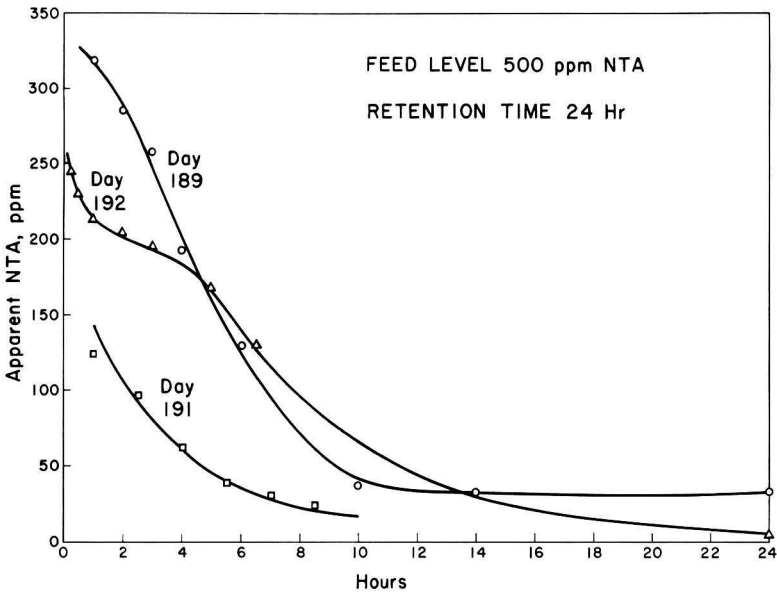


Figure 3. NTA die-away curves

Semicontinuous activated sludge unit fed 500 mg. per liter of NTA as sole organic carbon source, showing mg. per liter of apparent NTA in liquid phase at intervals during the 24-hour cycle, after 3 months' operation

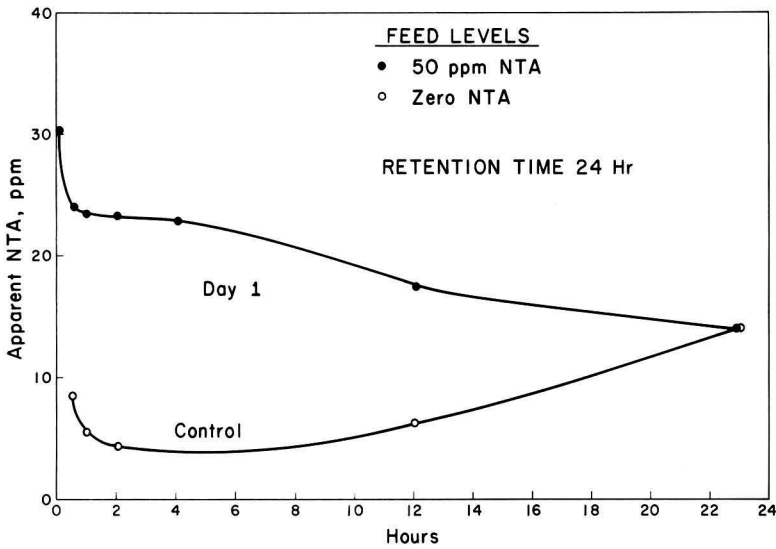


Figure 4. NTA die-away curves for first day of operation

Semicontinuous activated sludge units receiving standard feed plus zero (control) or 50 mg. per liter of NTA, showing mg. per liter of apparent NTA in liquid phase at various times during 24-hour cycle

daily by a modified Hellige methylene blue test (Swisher, O'Rourke, *et al.*, 1964) to detect any undegraded LAS. All effluents, from control and NTA units alike, almost always showed less than 0.1 mg. per liter of methylene blue-active substances (MBAS), indicating that the NTA did not interfere with the biodegradation action of the sludge. One major exception occurred when the continuous flow units were changed from 6-hour to 3-hour retention time. The control and the 20 mg. per liter NTA units both averaged about 1 mg. per liter of MBAS for 1 day and then dropped back to normal. The 200 mg. per liter NTA unit was upset considerably more, the effluent showing excess methylene blue reaction for about a week and reaching a maximum of about 4 mg. per liter on the fourth day. However, the NTA biodegradation in this unit remained better than 90% throughout (Figure 8).

On a few occasions the performance of the semicontinuous units was monitored by the COD analysis for total dichromate oxidizable organic content (American Public Health Association, 1960). There was no significant difference between the control and the 80 mg. per liter NTA units, both effluents averaging about 30 mg. per liter COD compared to 400 to 450 mg. per liter in the feeds.

In the activated sludge process a certain fraction of the organic nutrient, perhaps 10 to 50%, is converted to new sludge—i.e., bacterial cells—instead of being oxidized completely to carbon dioxide and water, depending on the exact

operating conditions (Busch and Myrick, 1961). Under the conditions of the present work the amount of newly synthesized sludge is estimated at 20 to 30% of the nutrient fed. This is greater than the loss of sludge in the effluent due to incomplete settling, resulting in a gradual increase in mixed liquor suspended solids and necessitating occasional removal of solids if the level is to be held in the desired range. Throughout this work there was no significant difference between the control units and the NTA units with respect to the net increase in solids, except when NTA was fed at 500 mg. per liter as the sole organic carbon source, discussed below.

Finally, no consistent effect on the settling rate of the sludge was attributable to the NTA, as observed in the continuous flow units. Settling was uniformly good at 6-hour retention time in the aerator ($1\frac{1}{2}$ -hour retention in the settler). At the 3-hour rate ($\frac{3}{4}$ hour in the settler) the sludge level in the 20 mg. per liter NTA unit was near the top of the settler for most of the 14-day period, and likewise in the control unit for several days. On the other hand, at the higher NTA level of 200 mg. per liter, the sludge settled well throughout. Such differences sometimes develop in units under supposedly identical conditions, and the effects, if any, of NTA on settling are evidently so small as to be obscured by unknown or uncontrolled variables.

NTA as the Sole Carbon Source. Pending the development of the analytical method for NTA a semicontinuous activated

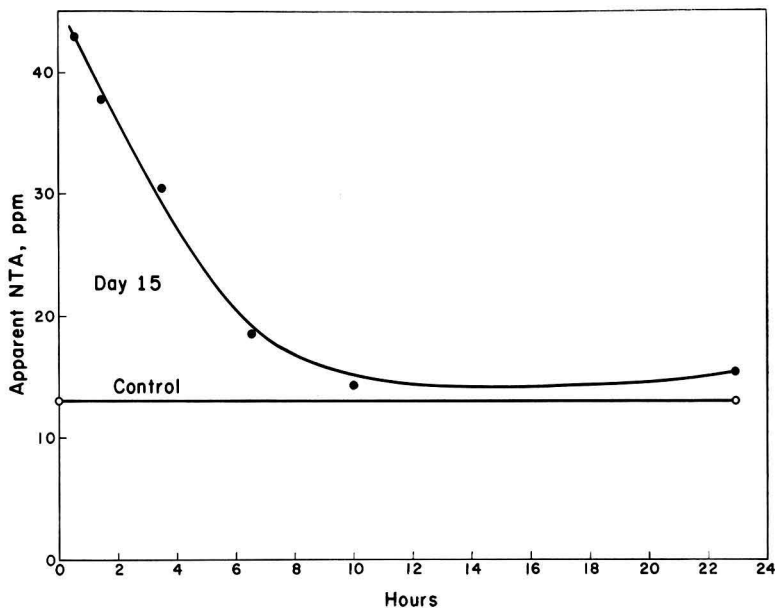


Figure 5. NTA die-away curves for 15th day of operation

See Figure 4 for conditions

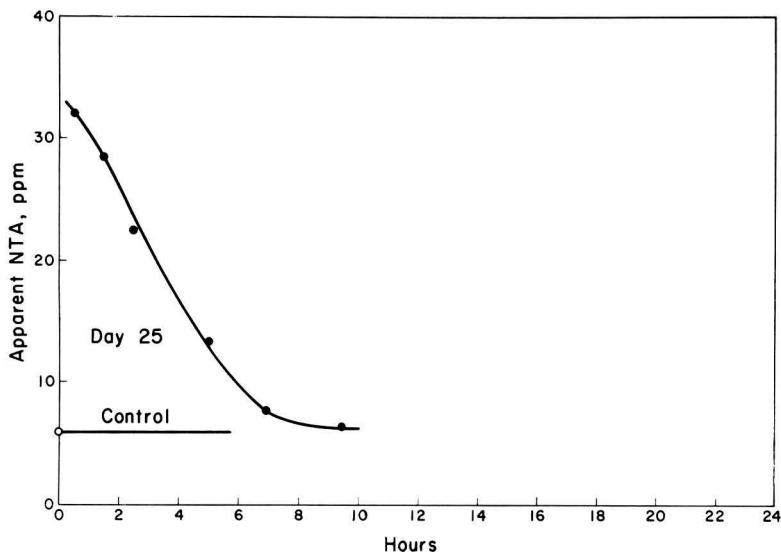


Figure 6. NTA die-away curves for 25th day of operation

See Figure 4 for conditions

sludge unit was put into operation, starting with fresh sludge and the standard feed plus an added 80 mg. per liter of NTA. During the next 3 months the NTA level was raised to 160, 250, 350, and finally 500 mg. per liter, with corresponding reduction in the amount of standard feed down to zero, and operation was continued at that final level for another 6 months. During this period the NTA served as the sole source of organic carbon, except for the small amount supplied by the 20 mg. per liter of LAS.

Operation of the unit was smooth throughout, and LAS removal was essentially complete, showing 0.05 to 0.15 mg. per liter of MBAS in the effluent compared to 0.05 in the control unit. During the first 3 months, the growth of mixed liquor suspended solids followed the pattern usually observed, the amount increasing from 2500 to 3000 mg. per liter within a week or two, solids being removed at that time to return it to 2500. During the last 6 months of operation, on NTA alone, the solids level held generally in the range of 1500 to 2000 mg. per liter without necessity for solids removal beyond the amount normally leaving the system suspended in the daily settled effluent. The sludge settled as well as or better than usual, reaching a volume of 100 ml. within $\frac{1}{2}$ hour.

It may thus be concluded that the nutritive value of 500 mg. of NTA is somewhat less than that of the 390 mg. of organic nutrients in the standard feed, so far as sludge synthesis is concerned. Nevertheless, there is no doubt that the NTA can serve as the sole source of organic carbon for the nutrition of the sludge, and hence that NTA is biodegradable.

NTA Biodegradation Rate. With the development of the chelometric analytical method, degradation rate studies became possible. The semicontinuous unit receiving 500 mg. per liter of NTA in its feed was sampled at intervals during the 24-hour cycle on three different occasions, with results as shown in Figure 3. Extensive degradation of the NTA is

clearly evident, although there is some discrepancy in detail between the individual die-away curves. These discrepancies may originate in the feeding, sampling, or analytical steps, or they may reflect actual day-to-day differences in the performance of the activated sludge itself. The latter possibility seems the more remote, because the feed level of NTA had been at 500 mg. per liter for about 3 months and there was no evident reason why steady state should not have been attained.

Further information on degradation rate was obtained at a lower NTA feed level and in the presence of natural organic nutrients. Two semicontinuous units were set up with laboratory sludge acclimated to LAS but not to NTA. Both were given the standard feed and one received 50 mg. per liter of NTA as well. After acclimation to the NTA had occurred, the disappearance of the NTA (Figures 5 and 6) closely paralleled the curves of the 500 mg. per liter unit (Figure 3). It is evident from Figures 4, 5, and 6 that considerable amounts of chelating material appear in the control unit, fed no NTA. This ranged from around 5 to 15 mg. per liter, a significant fraction of that found in the NTA unit. Since these values approach each other closely as the aeration proceeds, it is reasonable to assume that the interfering material is formed equally in both cases, and that the difference between the NTA unit and the control unit is at least a qualitative measure of the NTA present.

Judging by the curves of Figures 3 to 6, the degradation rate of NTA in the semicontinuous operation corresponds to half life of about 4 to 6 hours. From this one might anticipate perhaps 50 to 75% degradation in a continuous flow unit with 6-hour retention time, and 25 to 50% degradation in a 3-hour unit. In actual fact, the degradation is well over 90% at either rate, once acclimation has occurred.

The pertinent data are given in Figures 7 and 8 and Tables I and II. When 20 mg. per liter of NTA is fed, in no case

is there any significant difference from the control effluent, after acclimation has occurred. Even assuming the most unfavorable distribution of the standard deviation (Table II, days 16 to 49) the control effluent would be 1.5 mg. per liter and the NTA effluent 1.9, a difference of 0.4 mg. per liter, or 2% of NTA remaining, or 98% degradation. Assuming the opposite extreme, the degradation would be 104%. Feeding at 200 mg. per liter of NTA at 6-hour retention, after the initial acclimation the effluent first leveled off at about 15 mg. per liter and then trended downward to 3 mg. per liter at day 49, averaging 8.7. Corrected by the control these figures correspond to 92.5 and 99% degradation, average 96.5%. During 2 weeks' operation at 3-hour retention, effluent averaged 13.1 mg./liter of apparent NTA, 94% bio-degradation.

Thus the biodegradation rate in the continuous flow systems corresponds to a half life considerably less than 3 hours and is considerably faster than in the semicontinuous units.

Adsorption. In the area of LAS biodegradation the question has often been raised, and as often answered, as to whether LAS removal is by adsorption onto the sludge instead of by biodegradation. Suitable techniques are not yet developed for detection and analysis of adsorbed NTA, so this question cannot be answered directly for the case of NTA biodegradation. However, a simple calculation shows that, like LAS, removal of NTA by adsorption can account for only a minor fraction, if any at all, of the total removed, and thus that the major mechanism at work is biodegradation.

Consider, for example, the operation of the continuous flow unit during days 19 to 49, with 200 mg. per liter of NTA in the feed and 6-hour retention. Its working volume is 300 ml. and it received 1.2 liters of feed per day, containing 180 mg. of nutrient broth and allowing the synthesis of perhaps 18 to 90 mg. of new sludge per day. This amounts to 540 to 2700 mg. of new sludge formed during the 30 days which when added to the initial 1200 mg. in the system would make a total of say 2000 to 4000 mg. During this same 30 days, a total of 7200 mg. of NTA was fed and 270 left the system in the effluent. It is hardly reasonable that the remaining 6900 mg. was adsorbed on the 2000 to 4000 mg. of sludge, because in the first place no such increase in weight of the sludge was observed and in the second place the sludge, like any other adsorbent, could not be expected to adsorb more than 1 to 10% of its own weight. Thus little, if any, of the 6900 mg. of NTA could have been removed by adsorption, and we are left with biodegradation as the most likely mechanism.

Acclimation. The data show that a certain amount of acclimation time was necessary before the NTA degradation could proceed smoothly. There was some indication of this in the semicontinuous treatment, where the abnormal shape of the first day's curve compared to the two later curves (Figures 4 to 6) may be attributed to lack of acclimation. This unit had been started with a sludge already acclimated to laboratory operation, although not to NTA. In the continuous units, starting with fresh sludge acclimated neither to labora-

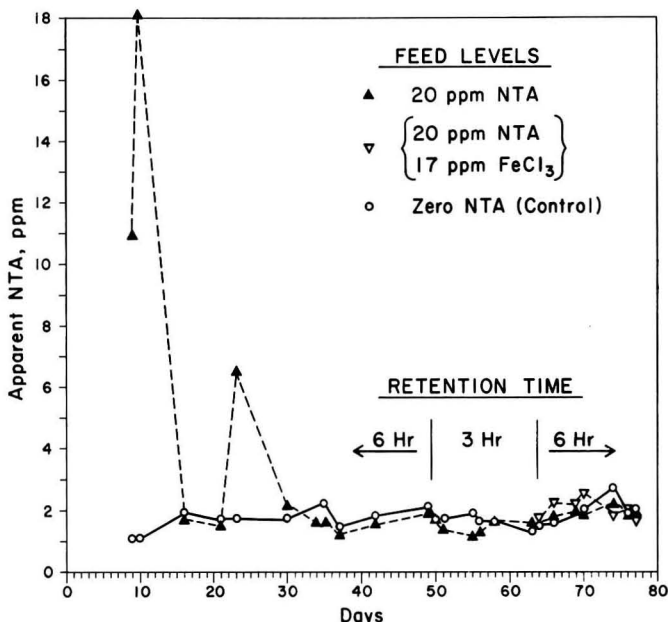


Figure 7. NTA biodegradation in continuous flow units

Apparent NTA content, mg. per liter, of effluents. Fed 20 mg. per liter of NTA

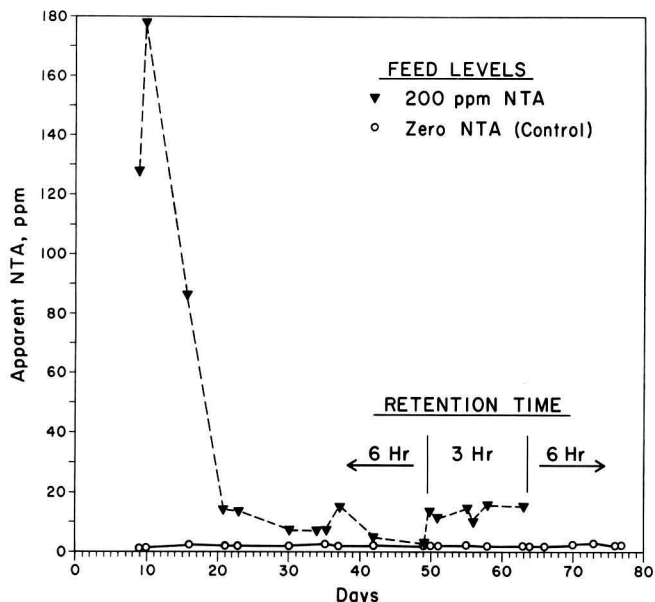


Figure 8. NTA biodegradation in continuous flow units

Apparent NTA content, mg. per liter of effluents. Fed 200 mg. per liter of NTA

tory operation nor to NTA, some 2 to 3 weeks was required before full degradation could be accomplished within the 6-hour retention time (Figures 7 and 8).

Bunch and Ettinger (1967) likewise found that NTA biodegradation required prior acclimation.

Biodegradation of NTA-Iron Complex. Presence of iron in a 1 to 1 ratio (1 atom of iron as FeCl_3 to 1 molecule of NTA) had no effect on the biodegradability. The comparison was made during days 63 to 77 (Figure 7) and Table II shows that there was no significant difference in the apparent NTA contents of effluents from NTA + Fe, NTA alone, or the control unit. This experiment gives no information as to whether the iron complex itself was degraded directly or whether the attack was on the free NTA in dissociative equilibrium with the iron complex at the ambient pH 7 to 8 of the sludge system.

Effectiveness of Continuous vs. Semicontinuous Treatment.

It is often assumed that the 24-hour semicontinuous biodegradation test procedure must necessarily have a biodegradation potential considerably greater than a continuous flow system with shorter residence time. The SDA test procedure has been criticized as giving unrealistically good results on this account. The present data show that this assumption and criticism are not necessarily valid, since the degradation rate of NTA is considerably faster in the continuous flow system under the conditions used. Similar results have also been obtained in the biodegradation of the benzene rings of LAS (Swisher, 1967).

This apparent anomaly probably arises from the shock loading of the semicontinuous system at each day's feeding, upsetting the sludge and requiring metabolic readjustments.

The continuous flow operation involves no such disturbances and under suitable steady-state operating conditions the efficiency may greatly exceed that of the semicontinuous system.

Acknowledgment

R. G. Schwartz and F. M. Smith were responsible for the daily care and operation of the activated sludge units, and for many of the NTA analyses.

Literature Cited

American Public Health Association, New York, "Standard Methods for the Examination of Water and Wastewater," 12th ed., pp. 510-14, 1965.
 Bunch, R. L., Chambers, C. W., *J. Water Pollution Control Federation* **39**, 181-7 (1967).
 Bunch, R. L., Ettinger, M. B., "Biodegradability of Potential Organic Substitutes for Phosphates," 22nd Annual Purdue Industrial Waste Conference, Lafayette, Ind., May 1967.
 Busch, A. W., Myrick, N., *J. Water Pollution Control Federation* **33**, 897-905 (1961).
 Pollard, R. R., *Soap Chem. Specialties* **42** (9), 58-62, 130-5 (1966).
 Soap and Detergent Association Subcommittee on Biodegradation Test Methods, *J. Am. Oil Chemists' Soc.* **42**, 986-93 (1965).
 Swisher, R. D., "Biodegradation of LAS Benzene Rings in Activated Sludge," 22nd Annual Purdue Industrial Waste Conference, Lafayette, Ind., May 1967.
 Swisher, R. D., O'Rourke, J. T., Tomlinson, H. D., *J. Am. Oil Chemists' Soc.* **41**, 746-52 (1964).

Received for review July 17, 1967. Accepted September 7, 1967. Division of Water, Air, and Waste Chemistry, 154th Meeting, ACS, Chicago, Ill., September 1967.

Gas Chromatographic Analysis of Polycyclic Aromatic Hydrocarbons in Soot Samples

B. B. Chakraborty and Ronald Long

Chemical Engineering Department, The University of Birmingham, Birmingham, England

■ A relatively rapid method of identifying and determining polycyclic aromatic hydrocarbons (p.c.a.h.) in soot samples has been developed. The individual hydrocarbons are determined by programmed temperature gas chromatography using dual flame ionization detectors. Peaks in the gas chromatogram are identified by comparing the relative retention times with those of pure hydrocarbons and by ultraviolet absorption spectrophotometry of the fractions separated by gas chromatography. A simple method of collecting these fractions and of ensuring that the detector sensitivity remains constant is described. Both normal and Hi-Pak packed columns have been employed. The analyses of soots from ethylene and ethane diffusion flames are given as examples.

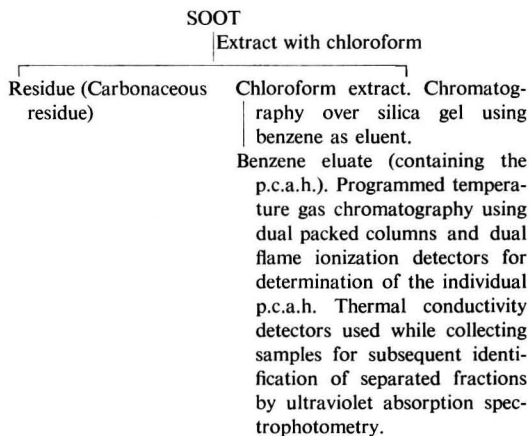
A rapid method for the identification and determination of the polycyclic aromatic hydrocarbons (p.c.a.h.) is important because these include carcinogens with which all city dwellers come into contact. Sawicki (1964) lists these carcinogens and materials in which they have been detected.

The analysis usually involves isolation as a class, with subsequent separation of the individual members. Three versions of chromatography—namely, column, paper, and thin-layer chromatography—have been used in the separation of the individual p.c.a.h. Identification and determination in the separated fractions have often been done spectroscopically, usually by ultraviolet absorption spectrophotometry (Sawicki, 1964). The procedure is, however, extremely tedious and the loss during analysis may, in certain cases, be as high as 50% (Hoffmann and Wynder, 1962a), although usually it is below 25% (Chakraborty, 1967).

The application of gas chromatography to separate the p.c.a.h. has been studied recently (Ettre *et al.*, 1964; Cantuti *et al.*, 1965; De Maio and Corn, 1966; Carugno and Rossi, 1967; Wilmhurst, 1965).

In the authors' investigation of the formation of the p.c.a.h. during incomplete combustion of hydrocarbons in diffusion flames (started in early 1965), a rapid method of identifying and estimating the individual p.c.a.h. present in soot formed under various conditions of hydrocarbon combustion was re-

quired. The procedure, which combines the specificity of ultraviolet absorption spectrophotometry with the rapidity of gas chromatography, is summarized as follows:



Isolation of P.C.A.H.

The soot (0.3 to 0.5 gram) is extracted with chloroform in a Soxhlet apparatus in an atmosphere of nitrogen. The presence of this inert atmosphere is essential; otherwise, the extract becomes incompletely soluble when redissolved in chloroform. After 8 hours of extraction, the fresh extract no longer fluoresces, or shows any color under ultraviolet light, indicating the absence of p.c.a.h.

After the extraction is complete, the bulk of the chloroform is distilled off from a water bath, and the residual chloroform is removed at room temperature by passing a current of nitrogen through it. This is necessary because certain lower p.c.a.h. such as phenanthrene and anthracene have an appreciable vapor pressure even at 100° C. (Commins, 1962). The extract thus obtained contains, besides the p.c.a.h., other substances—e.g., oxygen-containing compounds (Arthur and Napier, 1954; Thorp *et al.*, 1955; Meier zu Köcker, 1966). To isolate the p.c.a.h. as a class, this extract is subjected to

chromatography over silica gel. Before chromatography, the silica gel (M. F. C. Hopkins and Williams, Ltd., Chadwell Heath, Essex, England) is conditioned to adjust the moisture content to 3% using the method suggested by Cahmann (1957).

The chromatographic column (30 × 1 cm.) is packed by the usual wet method using benzene as the dispersing medium. The chloroform extract of soot is then transferred quantitatively to the top of the column by dispersing it in small volumes of benzene. The column is protected from light to prevent photodegradation of the p.c.a.h. during chromatography and is eluted with 100 ml. of benzene.

The bulk of the benzene is distilled off on a water bath in an atmosphere of nitrogen, and the residual benzene is removed by passing a current of nitrogen at room temperature. The material is then quantitatively transferred to a 1-ml. volumetric flask using carbon disulfide as the solvent (this gives no response with hydrogen flame detection). The carbon disulfide is evaporated at about 35° C., and a jet of nitrogen is allowed to play on the surface of the solution to expedite the evaporation.

To make sure that none of the p.c.a.h. is left in the column, it is (after elution with 100 ml. of benzene) washed occasionally with 100 ml. of a mixture of equal volumes of chloroform and methanol. The eluate, after evaporation of the solvents, is again chromatographed in a column of partially deactivated alumina (100- to 200-mesh, Peter Spence and Sons, Ltd., Widnes, England) containing about 13% moisture using cyclohexane with increasing amounts of ether as eluents. A number of fractions is thus collected using an LKB RadiRac fraction collector (cf. Cleary, 1962). These fractions are evaporated under vacuum at 50° C. and redissolved in spectroscopic grade cyclohexane (British Drug Houses) and the spectra are recorded by a double beam (Perkin-Elmer Model 137) ultraviolet spectrophotometer using 3-ml. cells of 1-cm. light path. The absence of any characteristic absorption band between the wavelengths of 200 and 430 m μ is taken as indicating the absence of any p.c.a.h.

Although control runs with synthetic mixtures were not made to determine the efficiency of recovery by the preliminary column chromatography, the above checks were made to make sure that all the polycyclics were eluted from the column when

benzene was used to elute them. It is perhaps safer, however, that the results be regarded as minimum values.

Analysis of Individual P.C.A.H.

The "aromatic fraction" (benzene eluate) dissolved in carbon disulfide is then analyzed using an F and M Model 810 dual column research gas chromatograph, equipped with dual flame ionization and dual thermal conductivity detectors, and having separate heaters for the injection port, detector blocks, and the column oven. Dual columns are necessary to avoid baseline drift during temperature programming (190° to 300° C.) due to bleeding of liquid phase. In the case of isothermal operation, the resulting background signal is constant and can be balanced out electrically, but during a programmed run, the vapor pressure of the liquid phase rises and more of it is carried to the detector.

For the quantitative determination of the p.c.a.h., the more sensitive flame ionization detectors are used. The optimum operating conditions are summarized in Table I.

In the following discussion, the columns mentioned above are described as "normal" columns.

For the quantitative determination of the p.c.a.h., the more common internal standard method cannot easily be used because of the complexity of the mixtures to be analyzed. This is evident from the chromatogram shown in Figure 1. The sensitivity of a flame ionization detector is dependent on the ratio of carrier gas-hydrogen-air flow rates. With the instrument used in the present work, it is difficult to reproduce exactly the flow rates and, therefore, the detector sensitivity. It is, therefore, necessary to resort to some auxiliary method of checking and keeping constant the detector sensitivity.

Procedure

The detector block and the injection port are allowed to stabilize at the temperatures of 370° and 350° C., respectively. Hydrogen, air, and helium flow rates are set approximately at the predetermined values given in Table I. The electrometer sensitivity is set at a predetermined value.

The column oven temperature is raised to the lower limit of 190° C. and allowed to reach equilibrium. A constant volume (5 μ L.) of a 0.08% (v./v.) solution of 1-methylnaphthalene in

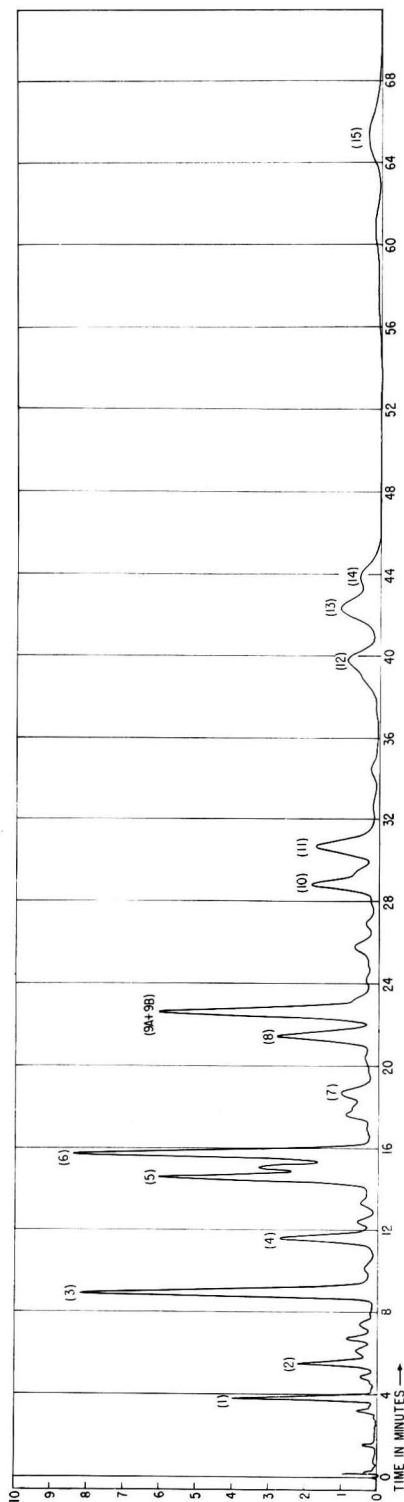


Figure 1. Gas chromatogram of a sample of aromatic fraction from soot under conditions given in Table I
Numbers of the peaks correspond to the compounds reported in Table II

dioxan is injected into the injection port of the analytical column. Usually, by varying the flow rates of carrier gas and hydrogen only, reproducible peak areas for this constant sample volume can be obtained. Relative retention times are not affected by varying the carrier gas flow rate. In any case, the ultraviolet spectrophotometric analysis provides an independent means of identifying peaks. Since 1-methylnaphthalene is a liquid at room temperature, a very accurate standard solution can easily be prepared using a Hamilton microsyringe.

The peak area is measured by multiplying the peak height by the width at half height. Calibration charts ($\mu\text{g. vs. peak area in sq. cm.}$) for various p.c.a.h. have been prepared under the conditions given in Table I for the concentration range required, the detector response being linear.

The "aromatic fractions" of soots are analyzed under the same conditions and with the detector sensitivity used in preparing the calibration charts. The amount of each component is expressed in milligrams per gram of dry soot. As an example, the amounts of the various p.c.a.h. formed from ethylene and ethane diffusion flames under given experimental conditions are quoted in Table II. The analyses depend upon the fuel used and the rates of flow of fuel and air in the diffusion flame apparatus employed. The experimental details are given by Chakraborty (1967).

Using the above method of setting the detector sensitivity, the relative error in the gas chromatographic analysis of pure samples of p.c.a.h. is of the order of 0 to 7% for the large to medium-sized peaks and up to 10% for very small peaks.

The individual peaks in a chromatogram are identified routinely by comparing their retention times relative to pyrene with those computed for the pure hydrocarbons; however, certain groups of hydrocarbons such as phenanthrene and anthracene; the methylphenanthrenes; the methylpyrenes; chrysene, benzo[a]anthracene, and triphenylene; benzo[k]fluoranthene and benzo[b]fluoranthene; benzo[e]pyrene; benzo[a]pyrene and perylene have relative retention times very close to one another and are difficult to resolve in "normal" columns. However, the presence or absence of each of these components can be confirmed by ultraviolet absorption spectrophotometry of the fractions separated by gas chromatography.

Sample Collection from Gas Chromatograph

Since flame ionization detectors normally destroy the whole sample injected, fraction collection is not possible using such detectors. Consequently, thermal conductivity detectors are used during fraction collection. In the instrument employed in the present work, the two detectors are located side by side and special adaptors are provided for connecting the exit end of the columns to the thermal conductivity detectors. Because of the relatively low sensitivity of these detectors, highly concentrated samples are used; the more sensitive flame ionization detectors are used in the quantitative work.

The gas chromatograph is run under standard conditions (Table I). The recorder is connected to the dual thermal conductivity detectors. When a peak is just being eluted (as shown by the response of the recorder), the exit port of the detector is cleaned quickly with an ordinary pipe cleaner soaked in chloroform to avoid any contamination from a previously eluted component. A stainless steel tube ($25 \times 0.3 \text{ cm.}$) in the form of an inverted L with Swagelok fittings at one end is then pressed against the exit port of the

Table I. Optimum Operating Conditions

Column details. Dual—12-foot × 0.25-inch, 10% SE-52 on 60- to 80-mesh Chromosorb W.	
Operating conditions:	
Helium flow rate, ml./min.	80 N.T.P.
Hydrogen flow rate, ml./min.	30 N.T.P.
Air flow rate, ml./min.	300 N.T.P.
Injection port temperature, ° C.	350
Detector block temperature, ° C.	370
Starting column oven temperature, ° C.	190
Final column oven temperature, ° C.	300
Program rate, ° C./min.	4
Chart speed, cm./hr.	76

Table II. Polycarbon Aromatic Hydrocarbons Identified and Amounts Estimated in Soots from Ethylene and Ethane Diffusion Flames under Similar Conditions

Ethylene flow rate—5.4 ml./sec. at N.T.P. Air flow rate—61.6 ml./sec. at N.T.P.
 Ethane flow rate—4.21 ml./sec. at N.T.P. Air flow rate—55.7 ml./sec. at N.T.P.

Peak No.	Polycyclic Aromatic Hydrocarbons	Amounts, Mg. per G. of Dry Soot	
		Ethylene	Ethane
1	Acenaphthylene	4.7	13.3
2	Fluorene
3	(Phenanthrene) (Anthracene)	5.5	12.9
4	Methylphenanthrenes	1.2	4.0
5	Fluoranthene	5.2	10.7
6	Pyrene	6.7	17.9
7	Methylpyrenes
8	Benzo[<i>mno</i>]fluoranthene	1.4	3.1
9A	{ Chrysene } { Benz[<i>a</i>]anthracene }	6.3	13.0
9B	(A pyrene derivative)		
10	{ Benzo[<i>b</i>]fluoranthene } { Benzo[<i>k</i>]fluoranthene }	2.3	5.5
11	{ Benzo[<i>e</i>]pyrene } { Benzo[<i>a</i>]pyrene } { Perylene }	2.9	8.7
12	Indeno[1,2,3- <i>cd</i>]pyrene
13	Benzo[<i>ghi</i>]perylene	2.7	6.5
14	Anthanthrene
15	Coronene
	Dry soot, g. per 100 g. carbon input in fuel	7.8	2.2

detector taking care that the connection between the Swagelok fittings and the detector exit port is reasonably gas-tight. The eluted component present in the carrier gas is bubbled through a column of cyclohexane contained in a test tube. The period of collection is guided by the response of the detector. When the elution of a peak is almost complete (as shown by the return of the recorder pen nearly to zero), the tube is disengaged from the exit port. After each collection, the inside of the tube is washed thoroughly with the cyclohexane contained in the test tube. The solution thus obtained is then scanned in the double beam ultraviolet spectrophotometer as mentioned earlier. The spectra of some of the separated fractions and of the corresponding pure p.c.a.h. (or mixtures thereof) are shown in Figures 2 to 7.

Using the thermal conductivity detector, two fractions were collected during the elution of the compounds responsible for peak 9 (of the chromatogram in Figure 1) and made it possible to separate peak 9 since this appeared as two incompletely resolved peaks (possibly owing to differences in thermal conductivity of the two fractions). Consequently, two separate fractions could be collected from what might appear to be one peak using the flame ionization detector. The ultraviolet spectra of the fractions collected are completely different and are shown in Figures 6 and 7.

Discussion

The p.c.a.h. identified in soots from both ethylene and ethane diffusion flames are listed in Table II. Acenaphthylene, fluorene, fluoranthene, pyrene, benzo[*mno*]fluoranthene, indeno [1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, and anthanthrene

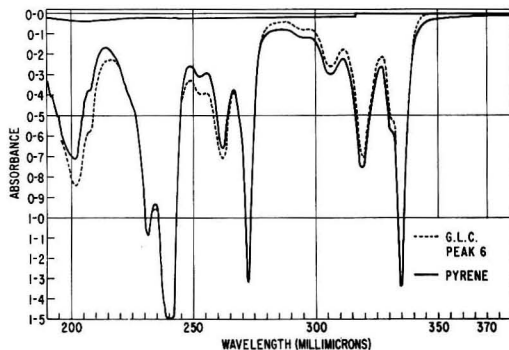


Figure 2. Ultraviolet absorption spectra of pyrene and that of gas chromatographic peak 6 in Figure 1

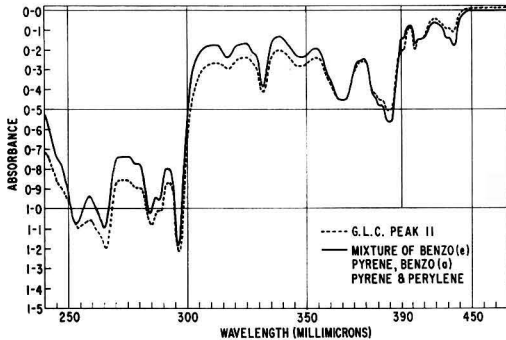


Figure 3. Ultraviolet absorption spectra of a mixture of benzo[e]-pyrene, benzo[a]pyrene, and perylene and of gas chromatographic peak 11 in Figure 1

can be separated fairly discretely by gas chromatography under the conditions mentioned in Table I, as revealed by the spectra of the separated hydrocarbons (Chakraborty, 1967). Typical spectra of the pyrene peak (peak 6 of Figure 1) and of pure pyrene, for example, are shown in Figure 2. But mixtures of phenanthrene and anthracene; the methylpyrenes; benzo[e]pyrene, benzo[a]pyrene, and perylene (Figure 3); the methylphenanthrenes (Figure 4); benzo[b]fluoranthene, benzo[k]fluoranthene, and possibly benzo[j]fluoranthene (Figure 5); and chrysene, benz[a]anthracene, and an unknown compound cannot be separated under these conditions. However, they can fairly easily be identified by comparing their spectra with those of mixtures of the pure hydrocarbons. Fortunately, the flame ionization detector response for the various hydrocarbons present in each of the above group of mixtures is approximately the same. Therefore, the amount determined from the area of the chromatographic peak on the basis of the major component (as revealed from the spectrum) represents the total amount of the mixed p.c.a.h. responsible for that particular peak.

The spectra of the gas chromatographically separated fractions correspond very well with those of mixtures of pure hydrocarbons (Figure 3). In certain cases, however, it has not been possible to make up mixtures of pure hydrocarbons which correspond exactly with the absorption maxima shown by the separated fractions (Figures 4 and 5).

The spectrum of a mixture of 1-methylphenanthrene and 2-methylphenanthrene matches fairly well with the spectrum of the gas chromatographically separated group of hydro-

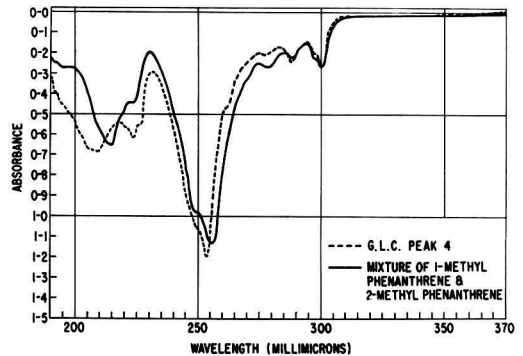


Figure 4. Ultraviolet absorption spectra of a mixture of 1-methylphenanthrene and 2-methylphenanthrene and of gas chromatographic peak 4 in Figure 1

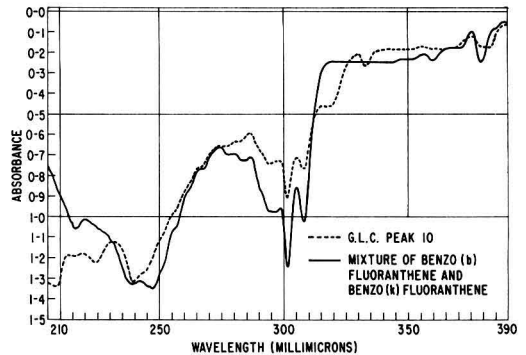


Figure 5. Ultraviolet absorption spectra of a mixture of benzo[b]-fluoranthene and benzo[k]fluoranthene and that of gas chromatographic peak 10 in Figure 1

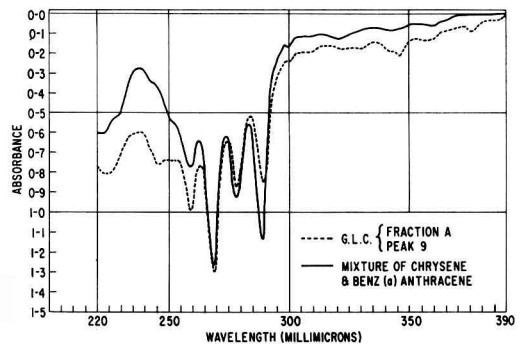


Figure 6. Ultraviolet absorption spectra of a mixture of benz[a]-anthracene and chrysene and that of fraction A of gas chromatographic peak 9

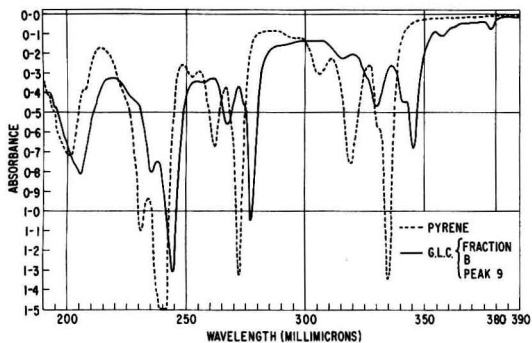


Figure 7. Ultraviolet absorption spectra of pyrene and that of fraction B of gas chromatographic peak 9

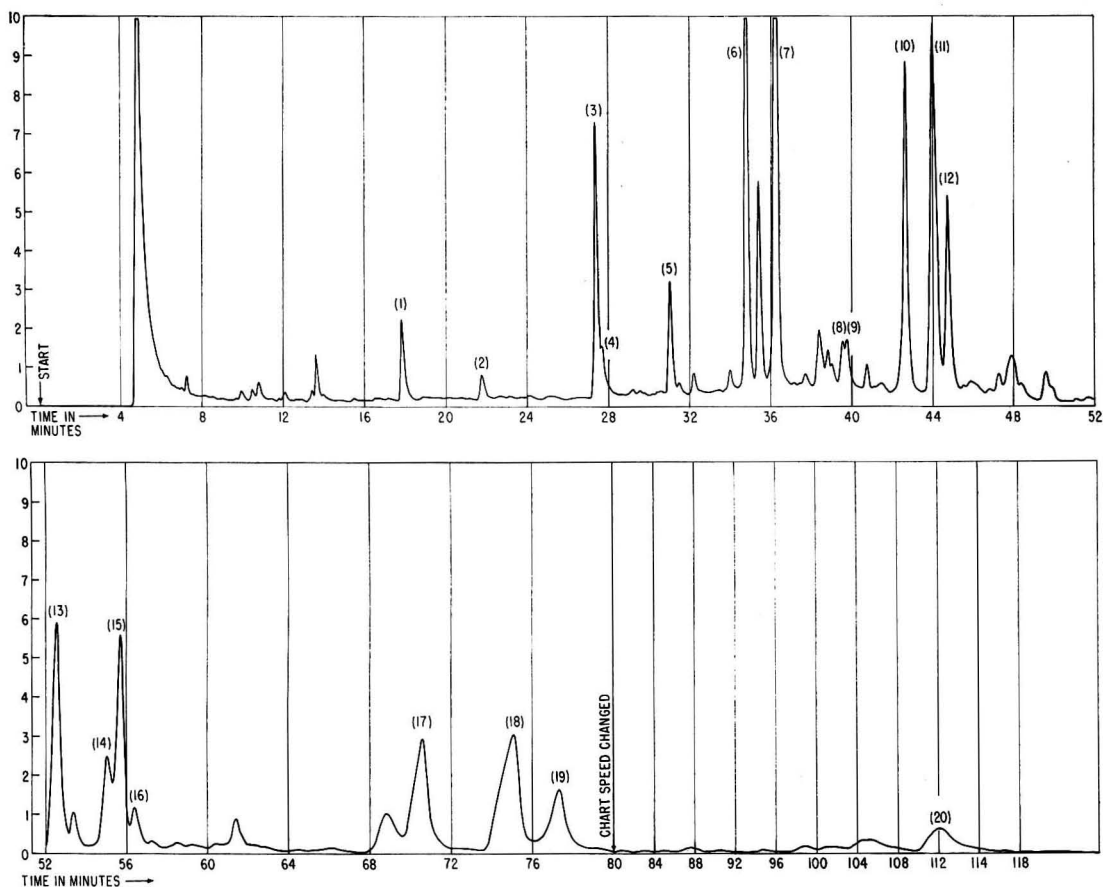


Figure 8. Gas chromatogram of aromatic fraction of soot using Hi-Pak columns under conditions given in Table III

(1) Acenaphthylene (2) Fluorene (3) Phenanthrene (4) Anthracene (5) Methylphenanthrenes (6) Fluoranthene (7) Pyrene (8) 1-Methylpyrene (9) 4-Methylpyrene (10) Benzo[*mno*]fluoranthene (11) Benzo[*a*]anthracene + chrysene (12) A pyrene derivative (?) (13) Benzo[*b*]fluoranthene + Benzo[*k*]fluoranthene + Benzo[*j*]fluoranthene (?) (14) Benzo[*e*]pyrene (15) Benzo[*a*]pyrene (16) Perylene (17) Indeno[1,2,3-*cd*]pyrene (18) Benzo[*ghi*]perylene (19) Anthanthrene (20) Coronene

Table III. Operating Conditions of Hi-Pak Column

Column details:

Analytical. 50-foot \times $\frac{1}{8}$ inch stainless steel column of SE-52.

Reference. same as given in Table I.

Operating Conditions:

Column oven temperature, ° C. Initial. 135 Final. 300

Column oven temperature program rate. 4° C./min.

Carrier gas flow rate, ml./min. 30 at N.T.P.

Hydrogen flow rate, ml./min. 30 at N.T.P.

Air flow rate, ml./min. 300 at N.T.P.

Other conditions are as given in Table I.

carbons (Figure 4). But the prominent absorption peak around 250 $m\mu$ is at a slightly shorter wavelength in the latter case. This may be due to the presence of some other derivatives of phenanthrene which absorbs strongly at 253 $m\mu$.

There is a striking resemblance (Figure 5) between the spectrum of a mixture of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene and that of the p.c.a.h. responsible for peak 10 of the chromatogram (Figure 1). In the latter spectrum, however, there are some further absorption peaks at 318, 333, and 383 $m\mu$ which are not present in the former. These absorption maxima correspond to certain of those of benzo[*j*]fluoranthene (cf. Badger *et al.*, 1966) which has a boiling point (480° C.) very close to that of benzo[*k*]fluoranthene (481° C.). The extra absorption maxima mentioned above are probably due to the presence of benzo[*j*]fluoranthene in the mixture.

Two fractions corresponding to peak 9 (of Figure 1) have been collected. The spectrum of the hydrocarbons responsible for fraction A compares very well with a spectrum of a mixture of chrysene and benz[*a*]anthracene (Figure 6). The spectrum given in Figure 7 (full lines) is due to the substance(s) responsible for fraction B. If this is compared with the spectrum of pyrene (dashed lines), a striking similarity in the α -, β -, and p -bands can be observed. But there is a bathochromic shift of all the absorption maxima. Therefore, it is very likely that the p.c.a.h. responsible for this spectrum is a derivative of pyrene; it could not, however, be identified; none of the p.c.a.h. so far reported in soots or smokes shows a spectrum similar to this.

As far as the authors are aware, methylphenanthrenes, benzo[*ghi*]fluoranthene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, indeno[1,2,3-*cd*]pyrene identified in soots from ethylene and ethane diffusion flames have not hitherto been reported in soots from diffusion flames. However, most of the p.c.a.h. identified in the present work, especially the major ones, have been shown to be present in diesel and automobile exhaust products and in air particulates (Hoffmann and Wynder, 1962b; Lyons, 1962). The concentrations in soots obtained from these sources are, however, considerably less than those in the present work.

In an attempt to achieve better resolution of the p.c.a.h., a Hi-Pak column (F and M Scientific Corp., Avondale, Pa.) of dimensions and under the conditions given in Table III has also been used.

Figure 8 represents a gas chromatogram using the Hi-Pak column for the sample whose chromatogram using a normal column is given in Figure 1. On comparing Figure 8 with Figure 1, it can be seen that certain mixtures such as phenanthrene and anthracene, benzo[*e*]pyrene, benzo[*a*]pyrene, and perylene, are revealed as separate components but are still incompletely resolved. The other previously mentioned mixtures cannot be resolved even by using the Hi-Pak columns. Moreover, changes in the flow rate of the carrier gas on programming the temperature lead to changes in sensitivity of the detector, so that the normal packed columns are preferred for routine analysis.

Capillary columns give better resolution of the p.c.a.h. (Cantuti *et al.*, 1965; Carugno and Rossi, 1967); however, they appear to be less suitable for routine quantitative analysis. While inlet splitters are available for capillary columns most of them tend to distort the concentrations of the components in the sample, particularly if the boiling range of the components is wide.

Acknowledgment

This investigation was supported, in part, by Public Health Service Research Grant AP 00323 from the National Center for Air Pollution Control. One of us (B.B.C.) expresses his gratitude to the Council of Scientific and Industrial Research, India, for the award of an Oil India Overseas Scholarship during the tenure of which this investigation was carried out. The authors thank C. P. Ward for preliminary advice.

Literature Cited

- Arthur, J. R., Napier, D. H., *Symp. Combust. 5th Pittsburgh* 1954, p. 303, Reinhold, New York, 1955.
Badger, G. M., Donnelly, J. K., Spotswood, T. M., *Australian J. Chem.* **19**, 1023-43 (1966).
Cahmann, H. J., *Anal. Chem.* **29**, 1307-11 (1957).
Cantuti, V., Cartoni, G. P., Libertini, A., Torri, A. G., *J. Chromatog.* **17**, 60-5 (1965).
Carugno, N., Rossi, S., *J. Gas Chromatog.* **5**, 103-6 (1967).
Chakraborty, B. B., Ph.D. thesis, University of Birmingham, Birmingham, England, February 1967.
Cleary, G. J., *J. Chromatog.* **9**, 204-15 (1962).
Commins, B. T., *Natl. Cancer Inst. Monograph No. 9*, 225-33 (1962).
De Maio, L., Corn, M., *Anal. Chem.* **38**, 131-3 (1966).
Ettre, L. S., Condon, R. D., Kabot, F. J., Cieplinski, E. W., *J. Chromatog.* **13**, 305-18 (1964).
Hoffmann, D., Wynder, E. L., *Cancer* **15**, 93-102 (1962a).
Hoffmann, D., Wynder, E. L., *Natl. Cancer Inst. Monograph No. 9*, 91-110, (1962b).
Lyons, M. J., *Natl. Cancer Inst. Monograph No. 9*, 193-9 (1962).
Meier zu Köcker, H., *Brennstoff-Chem.* **47**, 35-43 (1966).
Sawicki, E., *Chemist-Analyst* **53**, 24-26, 28-30, 56-62, 88-91 (1964).
Thorp, N., Long, R., Garner, F. H., *Fuel* **34**, S1-S13 (1955).
Wilhmurst, J. R., *J. Chromatog.* **17**, 50-9 (1965).

Received for review May 1, 1967. Accepted August 17, 1967.

Catalytic Combustion of Ethylene on Nickel Oxide

A. E. Cohen and Ken Nobe

University of California, Department of Engineering, Los Angeles, Calif. 90024

■ The catalytic combustion of ethylene with nickel oxide was studied in the temperature range of 260° to 370° C. and initial concentrations of ethylene ranging from 500 to 1200 p.p.m. The total gas flow was varied from 300 to 700 liters per hour (NTP). A simple power law rate equation with a reaction order of 0.65 correlated the experimental data. The experimental data and calculations of the effectiveness factors both indicated that below 350° C., pore diffusion had only a negligible effect on the combustion kinetics.

A number of investigations have been conducted in this laboratory on the combustion characteristics of copper oxide catalysts. The initial study was the complete oxidation of hexane on a copper oxide-alumina catalyst (Sourirajan, Accomazzo, *et al.*, 1961). Subsequently, a number of factors affect the performance of copper oxide catalysts—e.g., the method of preparing the catalyst from the same ingredients affects its activity for hydrocarbon combustion (Koutsoukos and Nobe, 1965). Pore diffusion effects have been shown to be significant for catalysts with rather small mean pore radii (Caretto and Nobe, 1966).

In the above studies, hydrocarbon concentrations were on the order of 1000 p.p.m. to approximate the concentrations in the exhausts of various combustion devices as in automobile engines and power plants. The importance of these studies, of course, is in the field of air pollution control which is rapidly gaining considerable attention from various segments of our technocratic society.

The investigation reported in this paper is the initial study comparing the combustion characteristics of nickel oxide catalysts with those of copper oxide. Pure nickel oxide catalysts were used to minimize the effects of pore diffusion. Since olefins are considered to be one of the more important hydrocarbon reactants in the formation of smog, the combustion of ethylene was studied.

Most of the work done on the catalytic oxidation of ethylene has been devoted to the study of the partial oxidation of ethylene to ethylene oxide. As an example, Twigg (1946), investigating the oxidation of ethylene on silver catalysts, observed that oxidation to ethylene oxide was achieved, but there was, in addition, a parallel reaction—i.e., the complete oxidation to CO₂ and H₂O. The reaction order for the complete combustion of ethylene was 0.3. Studies of olefin oxidation on CuO-carborundum catalysts by Belousov, Gorok-

hovatskii, *et al.* (1964) indicated that the oxidation reaction proceeds as olefin → aldehyde → CO₂ + H₂O, with a direct complete oxidation step in parallel. The investigation reported in this paper is limited to determining the effectiveness of the catalyst for the over-all reaction of ethylene to carbon dioxide and water. Excellent reviews of the literature on all aspects of catalytic hydrocarbon oxidation have been published (Dixon and Longfield, 1960; Margolis, 1963).

Experimental

The catalyst was prepared by precipitation of nickel hydroxide from nickel nitrate solution, using an amount of potassium hydroxide which was 30% above stoichiometric. The Ni(NO₃)₂ · 6H₂O (218 grams, 99.6% Baker analyzed reagent) was dissolved in 2.5 liters of distilled water. The solution was heated to 80° C. and stirred continuously. A solution of 127 grams of potassium hydroxide (Baker analyzed reagent) in 1.5 liters of distilled water was added dropwise to the warm nickel nitrate solution. The temperature was maintained at 80° C., and the solution was stirred continuously. The addition of the potassium hydroxide solution required about an hour. During this time, the solution slowly changed color from dark green (nickel nitrate) to light green (nickel hydroxide). The resulting mixture was stirred and kept at 80° C. for an additional 30 minutes. After the beaker was removed from the heater and allowed to cool for 20 minutes, the solution was filtered, and the precipitate was dispersed in 2 liters of distilled water and filtered. This procedure was repeated for an additional three washings. At the end of the four sets of washings, the wash solution was neutral.

The precipitate was dried overnight at room temperature and then forced into molds. Each mold was made of an aluminum plate 3 mm. thick with numerous 3-mm. I.D. holes. The molds were placed in an oven and heated for 16 hours at 220° C. After this heating, the color of the catalyst pellets changed from the green color of nickel hydroxide to the black color of nickel oxide. During the drying process, the pellet shrank. However, the dried pellets had good mechanical strength and were 2.5 mm. in diameter and 2.0 mm. in height.

Air from the campus supply line served as the carrier gas and oxidant. The air passed initially through a drying tube containing molecular sieve (Linde, 13X). The drying tube (35 × 5-cm. I.D.) contained 545 grams of the desiccant. The linear velocity of the air in the drying tube was approximately 6.1 cm. per second, and the inlet air was at room temperature. The same quality air was used to purge the desiccant of water vapor at 345° C. during regeneration. Under these operating

conditions, according to the manufacturer's specifications, the desiccant had to be changed every 10 hours to obtain less than 1.5 p.p.m. of water vapor and less than 50 p.p.m. of CO₂ in the air stream. To ensure that the water content of the air remained less than 1.5 p.p.m., the desiccant was changed at least every 8 hours. A calibrated rotameter was used to determine the air flow rate. The total flow rate was varied from 300 to 700 liters per hour (NTP). The flow rate of the ethylene was determined accurately with a soap bubble buret.

The catalytic reactor (Figure 1) was constructed from a borosilicate glass tube (60 cm. × 1.9-cm. I.D.). There were two sampling outlets and eight thermowells. The lower 35 cm. of the reactor was packed with glass rings which served as a gas mixer and preheater for the entering gas and as the support for the catalyst bed. Twenty grams of catalyst were placed on top of the glass rings.

Borosilicate glass tubing, 1-mm. O.D., was extended from the walls to the center of the reactor and served as thermowells for the iron-constantan thermocouples. The thermocouple wells were staggered in the reactor so that the axial and radial temperature gradients could be determined. A Honeywell recorder was used to monitor the reactor temperatures.

Power input to the catalyst bed and preheater was supplied by an electric furnace which enclosed the reactor tube. The furnace consisted of two sections, each equipped with a variable resistance control, to facilitate maintaining isothermal conditions within the catalyst bed.

The catalyst was activated in the reactor before the initial experimental run by passing air through the bed at 500 liters per hour and 400° C. for 48 hours.

The catalyst surface area and mean pore radii were determined after activation and at the end of this investigation. No measurable differences were noted. The BET surface area was 41.2 sq. meters per gram, and the mean pore radius was 272 Å.

The inlet and outlet ethylene concentrations were determined with a flame ionization detector unit. When the bed temperature and the outlet ethylene concentration achieved steady state for a given set of conditions, the outlet concentration and then the inlet value were measured. Carbon monoxide and carbon dioxide concentrations were determined with infrared analyzers.

Reproducibility runs were performed by periodically repeating several experimental points throughout this investigation. The catalytic activity remained constant during the entire experiment (~200 hours). The data were reproducible within ±2% of conversion.

Results and Discussion

Typical experimental results for the combustion of ethylene are shown in Figure 2 where the per cent conversion is plotted against the bed temperature; the total gas flow rate was maintained constant at 500 liters per hour (NTP), and the initial concentration of ethylene was varied from 500 to

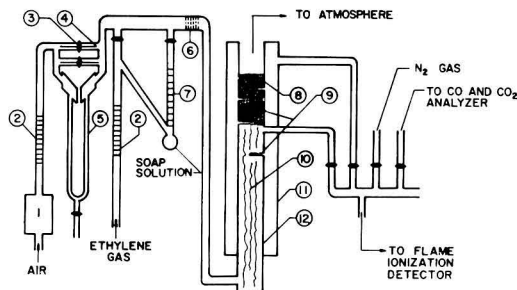


Figure 1. Apparatus

1, Molecular sieve. 2, Manometer. 3, Flowmeter. 4, Capillary tube. 5, Soap bubble buret. 6, Mixing disks. 7, Soap bubble buret. 8, Catalyst. 9, Thermowells. 10, Preheater. 11, Heating furnace. 12, Reactor tube

1200 p.p.m. The conversion of ethylene decreased with increasing initial concentration and increased with increasing temperature. For temperatures above 380° C., greater than 90% conversion was obtained.

The empirical rate equation,

$$r = kP^n \quad (1)$$

was used to represent the kinetics of ethylene combustion. A computer program was used to determine the empirical kinetic parameters from the experimental data, Equation 1, and the Arrhenius equation,

$$k = Ae^{-E/RT} \quad (2)$$

where the symbols have their usual meanings. In the computer program, the method of least mean squares was used to correlate the experimental data.

The empirical kinetic parameters for the catalytic combustion of ethylene and comparison between the kinetics of ethylene combustion on CuO, CuO-Al₂O₃, and NiO catalysts are given in Table I. The results of ethylene combustion on CuO-Al₂O₃ (Accomazzo and Nobe, 1965) and on pure CuO (Koutsoukos and Nobe, 1965) have been reported.

A reaction order of 0.65 was determined to give the best correlation of the data. The order was the same as for ethylene combustion on CuO. Figure 3 shows the Arrhenius plot for the catalytic combustion of ethylene on NiO. The points are the experimental data, and the continuous straight line was obtained from the computer calculations. As shown in this figure, there was good agreement between the calculations and the experimental data. However, a closer examination of the figure indicates that deviations between the experimental data and the linear calculated Arrhenius curve become evident at temperatures of about 350° C. and above. These deviations increase with increase in the reactor temperature and suggest that pore diffusion effects in the combustion of ethylene on the NiO catalysts begin to become significant above 350° C. Effectiveness factor calculations by the Thiele method as modified for fractional order reactions using the pseudo first-order reaction concept (Levenspiel, 1962) substantiate the experimental results indicating evidence of pore diffusion effects at about 350° C. Below this temperature, calculations of the effectiveness factor and the experimental data both indicated that the effects of pore diffusion in the kinetics of

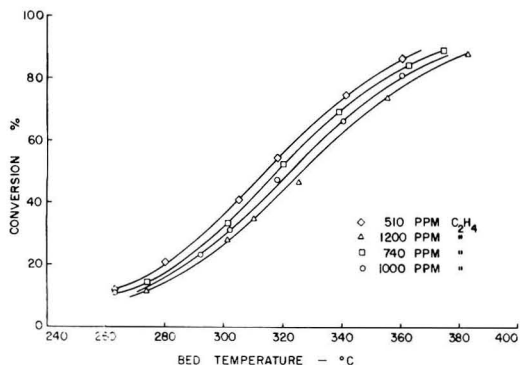


Figure 2. Catalytic combustion of ethylene on NiO
Flow rate = 500 liters/hour (NTP)

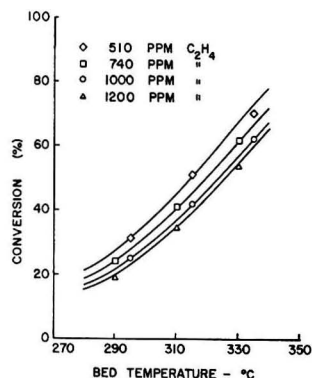


Figure 4. Calculated and experimental data for the combustion of ethylene on NiO

Flow rate = 500 liters per hour (NTP).
Points are experimental data and continuous curves are calculated data

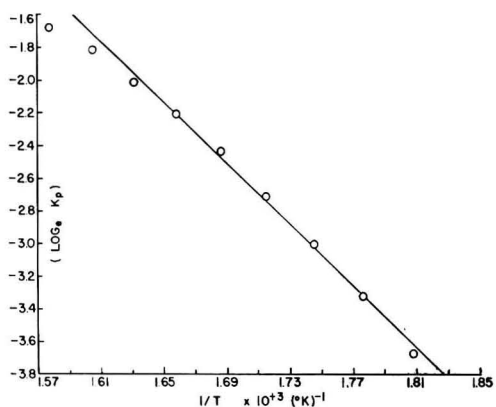


Figure 3. Arrhenius plot of combustion of ethylene on NiO

Table I. Catalytic Activity of CuO, CuO-Al₂O₃, and NiO for the Combustion of Ethylene

Catalyst	CuO	CuO-Al ₂ O ₃	NiO
Reaction order, n	0.65	0.50	0.65
Frequency factor (gram mole ethylene/hour gram catalyst atm. ^{<i>n</i>})	6.8×10^{10}	2.1×10^8	7.4×10^5
Activation energy (kcal./gram mole)	27.2	18.0	18.8
Reaction rate per gram at 1000 p.p.m. C ₂ H ₄ at 240° C., gram ethylene/(hour gram catalyst)	7.67×10^{-4}	1.65×10^{-4}	8.91×10^{-5}

ethylene combustion on the NiO catalysts were negligible. Furthermore, Thomas (1966), who recently studied ethane combustion on different size CuO-Al₂O₃ catalysts, showed that for his hydrocarbon-catalyst system, pore diffusion becomes significant above temperatures of about 350° C.

The results show (Accomazzo and Nobe, 1965) that external diffusion is not a significant factor in the oxidation kinetics at the reaction conditions encountered in this investigation. Since the nickel oxide catalyst used in this investigation was less active and had a larger mean pore radius than CuO-Al₂O₃ catalysts (by about a factor of 4), it seems reasonable to assume that below 350° C., mass transport of the ethylene to the external surface of the catalyst and in the pores did not affect the catalytic combustion kinetics of ethylene on NiO.

Figure 4 indicates the agreement between the calculated and the experimental values of the conversion of ethylene oxidation on nickel oxide at various temperatures. Figure 5 shows the calculated and experimental results describing the oxidation of ethylene at various flow rates. With the exception of the lowest flow rate, 300 liters per hour (NTP), there was good agreement between the calculated and experimental results. The flow rate of 300 liters per hour corresponded to a modified Reynold's number of 89 [$Re = Gd/\mu(1 - \epsilon)$]. Evidently, this deviation between the calculated and experimental results at 300 liters per hour was due to nonplug flow. Previously in this laboratory (Koutsoukos and Nobe, 1965; Accomazzo and Nobe, 1965), similar deviations at the low flow rates were observed. A more detailed discussion of the problem is given by Schwartz and Smith (1953) and Dorweiler and Fahien (1959).

The activities of the three different catalysts used in this laboratory in the studies of ethylene combustion are compared in Figure 6. The order of the catalysts' activity is $\text{NiO} < \text{CuO-Al}_2\text{O}_3 < \text{CuO}$. Although Yant and Hawk (1927) and Stein, Feenan, *et al.*, (1960) reported that NiO was a more active catalyst for hydrocarbon combustion than CuO , the investigations at the University of California indicate that the NiO is less active than CuO for ethylene combustion. These conflicting results, however, may be due to different methods of catalyst preparation (Koutsoukos and Nobe, 1965).

The results of this investigation indicate that although nickel oxide is not as effective a catalyst for the combustion of hydrocarbons as copper oxide, it is quite capable of completing the oxidation of the hydrocarbon to CO_2 and H_2O at reasonably low temperatures. Since copper catalysts have been effective in completely dissociating oxides of nitrogen (Ayen and Peters, 1962; Sourirajan and Blumenthal, 1961a, b; Wikstrom and

Nobe, 1965), it would be of considerable current interest to investigate the effectiveness of nickel catalysts for these reactions and for reactions between the nitrogen oxides and hydrocarbons.

Acknowledgment

The authors thank L. S. Caretto for development of the computer program.

Nomenclature

- A = Arrhenius frequency factor, gram mole/(hour)(gram catalyst)(atm. ^{n})
 d = $6/S$, mean particle diameter, cm.
 E = activation energy, cal./gram mole
 G = mass flow rate per unit cross-sectional area of bed, gram/(sq. cm.)(second)
 k = reaction rate constant, gram mole/(second)(gram)(atm. ^{n})
 n = reaction order
 P = partial pressure of ethylene, atm.
 Q = volume flow rate, liters/second (NTP)
 R = gas law constant
 r = reaction rate, gram moles/(gram)(hour)
 S = pellet surface area per pellet volume, cm.⁻¹
 T = temperature, ° C. or ° K.
 W = weight of catalyst bed, grams
 ϵ = catalyst bed porosity
 μ = viscosity, poise

Literature Cited

- Accomazzo, M. A., Nobe, Ken, *Ind. Eng. Chem. Process Design Develop.* **4**, 425-30 (1965).
 Ayen, R. J., Peters, M. S., *Ind. Eng. Chem. Process Design Develop.* **1**, 204-7 (1962).
 Belousov, V., Gorokhovatskii, J., Rubanik, M., *Kinetika i Kataliz* **3**, 221-9 (1962).
 Caretto, L. S., Nobe, Ken, *Ind. Eng. Chem. Process Design Develop.* **5**, 217-22 (1966).
 Dixon, J. K., Longfield, J. E., *Catalysis* **7**, 183-280 (1960).
 Dorweiler, V. P., Fahien, R. W., *A.I.Ch.E. J.* **5**, 139-44 (1959).
 Koutsoukos, E. P., Nobe, Ken, *Ind. Eng. Chem. Prod. Res. Develop.* **4**, 153-7 (1965).
 Levenspiel, O., "Chemical Reactor Engineering," p. 444, Wiley, New York, 1962.
 Margolis, L., *Advan. Catalysis* **14**, 429-501 (1963).
 Schwartz, C. E., Smith, J. M., *Ind. Eng. Chem.* **45**, 1209-18 (1953).
 Shapovalova, L., Gorokhovatskii, Rubanik, M., *Kinetika i Kataliz* **5**, 330-6 (1964).
 Sourirajan, S., Accomazzo, M. A., Nobe, Ken, *Actes Congr. Intern. Catalyses, 2nd, Paris, 1960* **2**, 2497-519 (1961).
 Sourirajan, S., Blumenthal, J. L., *Actes Congr. Intern. Catalyses, 2nd, Paris 1960* **2**, 2521-40 (1961a).
 Sourirajan, S., Blumenthal, J. L., *Intern. J. Air Water Pollution* **5**, 24-33 (1961b).
 Stein, K. C., Feenan, J. J., Thompson, G. P., Schultz, J. F., Hofer, L. J. E., Anderson, R. B., *Ind. Eng. Chem.* **52**, 671-4 (1960).
 Thomas, N. T., Department of Engineering, University of California, Los Angeles, unpublished results, 1966.
 Twigg, G., *Proc. Roy. Soc. London Ser. A* **188**, 92-141 (1946).
 Wikstrom, L. L., Nobe, K., *Ind. Eng. Chem. Process Design Develop.* **4**, 191-5 (1965).
 Yant, W. P., Hawk, C. O., *J. Am. Chem. Soc.* **49**, 1454-60 (1927).

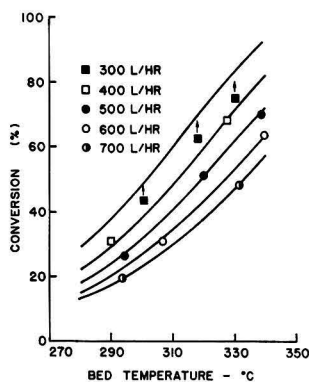


Figure 5. Calculated and experimental data for the combustion of ethylene on NiO

Initial concentration of ethylene = 750 p.p.m. Points are experimental data and continuous curves are calculated data

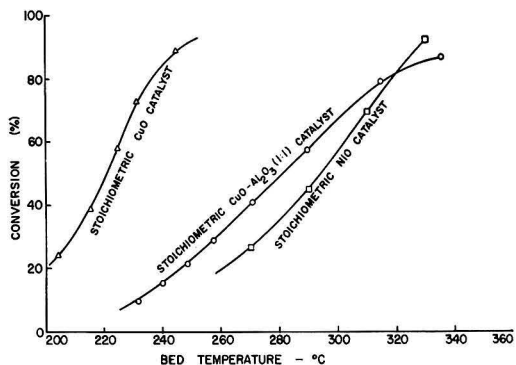


Figure 6. Comparison of catalytic activities of CuO , $\text{CuO-Al}_2\text{O}_3$, and NiO for ethylene combustion

Initial concentration of ethylene = 400 p.p.m., $W/Q = 0.04$ gram catalyst-hour/liter (NTP)

Received for review May 16, 1967. Accepted September 21, 1967. This work was supported by funds from the University of California Air Pollution research program.

Occurrence of Beryllium as a Trace Element in Environmental Materials

William R. Meehan and Lloyd E. Smythe

Australian Atomic Energy Commission, Private Mail Bag, Sutherland, New South Wales, Australia

Trace levels of beryllium were determined in a variety of environmental materials. Values for foodstuffs generally were low and were on the order of 0.01 to 0.10 p.p.m. Oyster flesh and mushrooms had the highest values. The highest values for human organs were found for lung. There was little evidence for any beryllium concentration mechanism in plants. Values generally were lower for soils than those previously reported. Water from the Indian Ocean showed the lowest value for sea waters. Rain water and river water contents were comparable. The beryllium content of fish samples showed that the gut of fishes had significantly higher levels than the flesh, and the levels were somewhat related to feeding habits.

Beryllium metal and its compounds now have extensive applications in atomic energy, space research, and in the chemical and metallurgical industries. The recognition that minute quantities of beryllium and its compounds, particularly beryllium oxide, can cause respiratory disease (White and Burke, 1955) led to the need for careful health control of factory and laboratory workers handling these materials. As a result of regular beryllium surveys resulting from such control, the analytical chemist has been called on to determine submicrogram quantities of beryllium in such diverse samples as paper smears, urine, grass, soil, effluent, rain water, river water, marine life, and air samples. In addition, the distribution of beryllium has been the subject of a number of geochemical and medical investigations. Recent reviews of the now extensive literature on the subject have been undertaken by Smythe and Whitem (1961) and Smythe and Florence (1963). Everest (1964) reviewed the general chemistry of beryllium.

A significant proportion of the earlier work on environmental trace element levels of beryllium used methods which

lacked the sensitivity and precision of those developed within the past four to five years. A knowledge of the environmental distribution and occurrence of beryllium is particularly useful to biologists, geochemists, medical research workers, and others involved in studies of the role of trace elements.

Very few results of surveys for traces of beryllium find their way into the literature where they can be used by research workers. Also, gaps exist in the range of materials covered, little work having been done, for example, on human organs and marine life.

Method

This study reports results for a wide range of materials using a reliable method for the determination of beryllium at sub parts per million levels (Cosgrove, Morgan, *et al.*, 1961). The method is based on the fluorimetric determination of beryllium in alkaline solution with morin (2',4',3,5,7-pentahydroxyflavone) following the work of Sill and co-workers (Sill and Willis, 1959; Sill, Willis, *et al.*, 1961). The morin method for beryllium constitutes the most sensitive chemical method known for this element, with a practical limit of 2×10^{-5} $\mu\text{g. Be per ml.}$

Details of preparation, digestion, and ashing of the solid samples have been described (Cosgrove, Morgan, *et al.*, 1961). The beryllium in aqueous samples was coprecipitated with ferric hydroxide, digested with perchloric acid, and extracted with acetyl acetone prior to the morin determination (Cosgrove, Morgan, *et al.*, 1961).

Results

A survey of the literature revealed a number of values for natural levels of beryllium in various samples (Table I).

The results of the present study are summarized in Table II. The choice of materials was governed by the gaps in the literature and the ready availability of samples. The main classes of materials examined were foodstuffs, human organs, plants, soils, waters, and marine life.

Table I. Levels of Beryllium from Previous Analysis

Source of Sample	Be Content, P.P.M. ^a	Reference
Talc	6.5×10^{-2}	Sill, Willis, <i>et al.</i> , 1961
Asbestos	2.4×10^{-1}	
Kaolin	7.4	
Monazite	5.9×10^{-2}	
Clays and coals of the Moscow basin	7.1	Volkov, 1962
Stream sediments—Oslo region, Norway, from 146 stream basins	2.3	Brinck and Hofmann, 1964
Seawater	10^2 to 10^{-3} $\mu\text{g. per liter}$	Lal, Arnold, <i>et al.</i> , 1964
Honey	Spectrographically present	Makerochkin and Udenich, 1960
Blood cells of <i>Ascidella aspersa</i>	60 $\mu\text{g. per liter}$	Rezaeva, 1964
Bottom muds of Indian Ocean	Be was detected in a few samples	Katchenkov and Flegentova, 1964
Alkaline rocks of the Ditrau massif	Be was present in very small amounts, and its content did not depend on the nature of the rocks	Ianovici and Ionescu, 1964
Granite rocks of the eastern Vitem highland (northwestern Trans-baikal) region	Proteozoic and Paleozoic granite, rocks: 1.2 to 7.6 Rocks of Mesozoic Intrusive Complex: 40 to 82	Zilov, Kusnetsova, <i>et al.</i> , 1963
Igneous rocks	Mafic: <1 Silicic: 6.5 Alkalic: 11.4	Shawe and Bernold, 1964
Sediment of the Sea of Azov	>10 to 30	Aleksandrov and Reznikov, 1964
Coal ash	300	Mason, 1952
Earth's crust	6	
Oilfield waters	20 to 200 $\mu\text{g. per liter}$	Collins and Pearson, 1964
Urine	0.05 $\mu\text{g. per liter}$ (limit)	Sutton, 1963
Ocean water	5×10^{-4} $\mu\text{g. per liter}$	Merrill, Lyden, <i>et al.</i> , 1960
Igneous rocks	2	Rankama, 1956
Meteorites (including chondrites and achondrites) (except U.S.A.)	0.038	Sill and Willis, 1962
Silicic volcanic glasses (western United States, southern Idaho), or Pearlette ash (member of the Sappa formation)	7.4	Griffitts and Powers, 1963
Cascade Range	4.4	
	Be Determined by Method Indicated	
	Chem. Analysis	Direct Reading Spectrograph
Beryl concentrate	4.04×10^4	4.0×10^4
Medium grade beryl ore	1.99×10^4	1.90×10^4
Low grade beryl ore	0.50×10^4	0.42×10^4
Tailing waste	0.094×10^4	0.086×10^4
Humans—	Be demonstrable in 20 of 58 cases	
Suspected berylliosis	Av. = 282 Min. = 8 Max. = 1925 } γ per gram of dried lung wt.	
Normal lung tissue—		
Cincinnati	0.00033 γ per gram	
Chicago	0.324 γ per gram	Schepers, 1962

^a P.p.m., unless otherwise noted.

Table II. Levels of Beryllium in Environmental Materials

Sample	Survey Figures (P.P.M. Ash Wt.)			
	Beryllium Level ^a		Ash, Fresh Wt., %	No. of Samples
	Range	Average		
Foodstuffs				
Beans (Lucas Heights area)	N.D. to 0.01	0.01	0.65	3
Cabbage (Lucas Heights area)		0.03	0.78	1
Hen eggs				
Yolk		0.01	1.75	1
Yolk + whites		0.006	1.01	1
Shells		0.014	77.44	1
Milk				
All samples	N.D. to 0.09	0.02	0.83	50
Lucas Heights area	N.D. to 0.04	0.02	0.81	17
Hawkesbury and Campbelltown	N.D. to 0.09	0.02	0.86	33
Mushrooms				
Lucas Heights area		0.12	1.32	1
Nuts				
Peanut kernels	0.01 to 0.03	0.02	2.6	2
Peanut shells	0.41 to 0.52	0.47	2.5	2
Almond kernels		0.01	2.9	1
Almond shells		0.01	2.9	1
Tomatoes (Lucas Heights area)		0.02	1.05	1
Yeast (bakers)		0.02	1.62	1
Aluminum (cooking saucepans)		N.D.	...	1
Human Organs				
Lung	0.05 to 0.34	0.21	0.6	4
Brain	0.05 to 0.10	0.08	1.3	3
Kidney	0.06 to 0.07	0.07	0.06	2
Spleen	0.05 to 0.09	0.07	0.07	2
Liver	0.03 to 0.06	0.04	1.1	2
Muscle	0.01 to 0.06	0.04	0.4	2
Vertebrae	0.01 to 0.11	0.04	9.1	5
Heart	0.01 to 0.06	0.03	1.4	3
Bone		0.02	9.5	1
Hair—(head)				
Lucas Heights, composite	0.61 to 1.20	0.93	2.7	5
Lucas Heights active areas (including Be working areas)	0.81 to 1.56	1.22	2.6	3
Away from Lucas Heights	0.25 to 0.56	0.48	4.3	6
Plants, etc.				
Acacia	} Sydney area	0.10 to 1.06	0.46	6
Angiosperms		0.15 to 2.00	0.69	5
Field lupine seeds			0.02	2.9
Grass				
All samples	0.01 to 0.96	0.32	4.6	96
Lucas Heights	0.06 to 0.56	0.26	4.5	18
Away from Lucas Heights	0.01 to 0.96	0.35	4.7	78
Tobacco				
Cigarette tobacco		0.25	11.0	1
Pipe tobacco		0.24	11.1	1
Cigarettes (manufactured)	0.24 to 0.26	0.25	13.1	2
Soil				
All samples	0.01 to 1.69	0.28		29
Lucas Heights	0.01 to 0.30	0.16		7
Lucas Heights (disposal ground)	0.08 to 0.75	0.32		3
Non-Lucas Heights	0.01 to 1.69	0.32		19

^a N. D. = not detected.

(continued)

Table II. Continued

Sample	Survey Figures (P.P.M. Ash Wt.)			
	Beryllium Level ^a		Ash, Fresh Wt., %	No. of Samples
	Range	Average		
Sand, Woronora R.				
All samples	N.D. to 1.67	0.21		65
Lucas Heights area	0.04 to 1.67	0.39		16
Other sites	N.D. to 0.57	0.15		49
Diatoms				
Kieselguhr G (from E. Merck, H. G. Darmstadt)		0.31		1
Phosphate rock				
Nauru	0.08 to 3.75	1.07		6
Marine				
Crabs				
Woronora R.	0.07 to 0.13	0.10	15.4	6
Non-Woronora R.		0.17	15.4	1
Eels		N.D.	5.0	1
Whole fish				
Woronora R.,				
Mullet	0.03 to 0.36	0.21	5.2	8
Blackfish	0.08 to 0.39	0.23	4.6	4
Non-Woronora R., mullet		0.01		1
Fish gut				
Woronora R.,				
Mullet	0.42 to 0.71	0.54	9.2	6
Blackfish	0.46 to 1.78	0.99	5.6	5
Leather jacket	0.48 to 0.63	0.56	3.2	2
Non-Woronora R.,				
Mullet	0.04 to 1.33	0.43	4.2	4
Blackfish	0.80 to 1.25	1.03	5.7	2
Fish fillets				
Woronora R.,				
Mullet	N.D. to 0.07	0.04	3.7	2
Blackfish		0.01	3.6	1
Perch and bream		N.D.	3.7	1
Non-Woronora R.,				
Blackfish	0.01	0.01	4.4	2
Bonita		0.01	2.4	1
Perch		0.01	1.6	1
Redfin		0.01	5.7	1
Mullet		0.02	3.3	1
Homosira Banks II				
Bubble-weed (coast south of Sydney)	0.01 to 0.05	0.03	16.5	5
Catostylus Mosaicus (jelly blubber)		N.D.	1.2	1
Oyster flesh				
All samples	0.01 to 0.27	0.03	2.0	59
Woronora R.	0.02 to 0.14	0.03	2.0	41
Hawkesbury R.	0.01 to 0.27	0.10	2.0	18
Oyster liquid				
All samples	0.01 to 0.03	0.02	2.7	2
Woronora R.	0.01 to 0.03	0.02	2.5	2
Hawkesbury R.		0.02	2.9	1
Oyster shells				
All samples	0.01 to 0.08	0.04	94.9	20
Woronora R.	0.01 to 0.08	0.04	93.8	14
Hawkesbury R.	0.02 to 0.06	0.04	96.5	6

Table II. Continued

Sample	Survey Figures (P.P.M. Ash Wt.)		Ash, Fresh Wt., %	No. of Samples
	Beryllium Level ^a			
	Range	Average		
Plankton preparations		N.D.	13.5	1
Prawns (green)		0.03	3.5	1
Cunjevoi flesh, Pyura Stoloniferra				
Mixture from Cronulla and Coalcliff		0.53	3.6	1
Cronulla	0.10 to 0.26	0.18	9.1	2
Coalcliff		0.42	4.1	1
Cunjevoi tunics, Pyura Stoloniferra				
Mixture from Cronulla and Coalcliff		0.30	35.4	1
Cronulla	0.05 to 0.08	0.07	38.5	2
Coalcliff		0.26	33	1
River Solid Particles				
Woronora (Discharge Pt.)		N.D.		1
Woronora (Tolofin)		N.D.		1
Rockweeds (algae)				
Cronulla		0.01	4.2	1
Coalcliff	0.02 to 0.54	0.28	5.2	2
Scallops, Tasmanian		0.02	1.7	1
Seaweed, Woronora R.	0.29 to 1.02	0.66	5.5	3
Shellfish flesh				
Mixture from Cronulla and Coalcliff		0.04	8.8	1
Cronulla	0.07 to 0.09	0.08	8.1	2
Coalcliff	0.30 to 1.15	0.73	14.0	2
Shellfish shells				
Cronulla	N.D. to 0.01	0.01	96.4	2
Coalcliff	N.D. to 0.01	0.01	96.3	2
Starfish, whole, Coalcliff		0.02	37.1	1
Zostera				
All samples	0.28 to 1.12	0.60	5.5	28
Woronora R.	0.28 to 1.12	0.61	5.5	27
Hawkesbury R.		0.41	5.5	1
			µg. per liter	
Waters				
Rain				
All samples	0.01 to 0.18	0.07		20
Lucas Heights	0.01 to 0.07	0.05		5
Non-Lucas Heights	0.03 to 0.18	0.08		15
River				
Lachlan (Forbes)		0.01		1
Macquarie (Bathurst)		0.01		1
Nepean (Emu Plains)		N.D.		1
Woronora (Discharge Pt.)	0.01 to 0.12	0.03		27
Woronora (Tolofin)	0.01 to 0.08	0.02		26
Sea				
Pacific Ocean		0.002		1
Indian Ocean		0.001		1
Tank				
Lucas Heights area	0.002	0.002		2

^a N.D. = not detected.

Locations of sampling sites may be seen in any general map of the state of New South Wales, Australia.

Discussion

Comparisons between the tables should be made only after considering the preparation and chemical analysis method used for each sample.

Results indicate the distribution of beryllium as a trace element in part of the local (Australian) environment. Possibly, samples from other regions in Australia or elsewhere in the world would result in different values.

Some general comments on the values in Table II are necessary.

Foodstuffs (Including Edible Marine Life). Values are generally low and lie in the range 0.01 to 0.10 p.p.m. Oyster flesh and mushrooms have the highest value.

Human Organs. The highest values were recorded for human lung.

Hair. Since the determinations were carried out on unwashed hair samples, the major part of the beryllium content may result from external contamination such as dust, smog, and hair preparations. The values are among the highest recorded in the survey.

Plants. Consistently high values in the range 0.25 to 0.50 p.p.m. give little evidence of any concentration mechanism in plants. Approximately the same levels of beryllium were found in the various forms of tobacco.

Soils and Rocks. Values are generally lower for soils than those previously reported. Only two values are reported for other geological materials (phosphate rock and kieselguhr).

Water. Seawater from the Indian Ocean showed the lowest value. Rain water and river water contents are comparable, but an exception was found in samples of tank water (collected from roofs of houses and stored in a galvanized iron tank). In tank water, fine sediment would have settled before the sample was taken, whereas suspended material would be present in rain water and river water samples.

Marine Samples. The fish samples are of some interest. At first, determinations indicated that different parts of the fish (flesh *vs.* organs) had markedly different beryllium contents. The beryllium content of the gut of fishes showed significantly higher levels, and the level was somewhat related to feeding habits of the fish. For example, *Girella tricuspidata* (blackfish) feeds on *Zostera* which contains relatively high levels of beryllium. *Mugil dobula* (mullet) and *Pseudomonacanthus ayraudi* (leather jackets) do not feed on this material, and consequently showed lower levels of beryllium in the gut. Results for fish flesh showed levels of beryllium comparable with other marine life. The levels of beryllium in cunjevoi and shellfish flesh from the Coalcliff area appeared to be higher than in other areas. This may be related to seepage of ground waters which contact numerous near-surface coal seams. The ground waters enter the tidal zone in this region.

No survey of the beryllium content of these coal seams has been carried out, but it has been reported by Volkov (1962) that some coals have appreciable levels of beryllium.

Acknowledgment

Thanks are due to John Loewenthal, G. M. Watson, and F. B. Bartholomew for the provision of some samples.

Literature Cited

- Aleksandrov, A. R., Reznikov, A. P., *Okeanologiya* **4** (4), 651-3 (1964) (CA **62**, 362g).
- Brinck, J. W., Hofmann, A., *Econ. Geol.* **59** (1), 79-96 (1964) (CA **60**, 13053h).
- Collins, A. G., Pearson, C. A., *Anal. Chem.* **36** (4), 787-9 (1964).
- Cosgrove, J. D., Morgan, J., Pakalns, P., *Australian At. Energy Comm. Rept. TM87* (1961).
- Everest, D. A., "The Chemistry of Beryllium," Elsevier, New York, 1964.
- Griffitts, W. R., Powers, H. A., *U. S. Geol. Surv. Profess. Papers*, **475-B**, 18-19 (1963).
- Helz, A. W., Annell, C. S., *U. S. Geol. Surv. Profess. Papers*, **424-C**, 380-2 (1961).
- Ianovici, V., Ionescu, J., *Akad. Nauk SSSR Tr. Geokhim. Konf.* **2**, 341-8 (1964) (CA **62**, 8883g).
- Katchenkov, S. M., Flegentova, E. I., *Tr. Vses. Nauchn. Issled. Geologorazved. Inst.* **1964** (227), 202-11 (CA **62**, 5096e).
- Lal, D., Arnold, J. R., Somoyajube, B. L. K., *Geochim. Cosmochim. Acta.* **28** (7), 1111-17 (1964) (CA **61**, 11756c).
- Makerochkin, B. A., Udenich, D. M., *Pchelovodstvo* **37** (11), 34 (1960) (CA **61**, 9962b).
- Mason, B., "Principles of Geochemistry," Wiley, New York, 1952.
- Merrill, J. R., Lyden, J. F., Honda, M., Arnold, J. R., *Geochim. Cosmochim. Acta.* **18**, 108 (1960).
- Rankama, T., "Isotope Geology," Pergamon Press, New York, 1956.
- Rezaeva, L. T., *Zh. Obshch. Biol.* **25** (5), 347-56 (1964) (CA **62**, 3129h).
- Schepers, G. W. H., *Diseases Chest* **42**, 600-7 (1962).
- Shawe, D. R., Bernold, S., *U. S. Geol. Surv. Profess. Papers*, No. **501, B100-B104** (1964) (CA, **62**, 364b).
- Sill, C. W., Willis, C. P., *Anal. Chem.* **31**, 598-608 (1959).
- Sill, C. W., Willis, C. P., Hygare, J. K., *Anal. Chem.* **33** (12), 1671-84 (1961).
- Sill, C. W., Willis, C. P., *Geochim. Cosmochim. Acta* **26**, (14) 1209 (1962).
- Smythe, L. E., Whittier, R. N., *Analyst* **86**, 83-94 (1961).
- Smythe, L. E., Florence, T. M., *Progr. Nucl. Energy, Ser. IX*, Vol. **3**, Chapt. 5, Pergamon Press, New York, 1963.
- Sutton, D. C., *U. S. At. Energy Comm. HASL*, 134 (1963).
- Volkov, K. Y., *Materialy po Geol. i Polezn. Iskopuemym Tsent. Raionov Evropeiskoi Chasti SSSR, Moscow, Sb* **1962** (5), 183-4 (CA **59**, 8492h).
- White, D. W., Burke, J. E., Eds., "The Metal Beryllium," The American Society for Metals, Cleveland, Ohio, 1955.
- Zilov, A. R., Kusnetsova, A. I., Cherenko, A. I., *Akad. Nauk. SSSR Sibersk. Otd.* **1963** (13), 145-52 (CA **62**, 7534h).

Received for review July 10, 1967. Accepted October 1, 1967.

Photooxidation of Formaldehyde at Low Partial Pressures of Aldehyde

T. C. Purcell and I. R. Cohen

National Center for Air Pollution Control, U. S. Department of Health, Education, and Welfare, 4676 Columbia Parkway, Cincinnati, Ohio 45226

■ The oxidant produced by the photooxidation of formaldehyde at low partial pressures of aldehyde has been identified as hydrogen peroxide. The apparent molecular imbalance between the peroxide formed and the formaldehyde consumed is attributable, at least in part, to surface effects related to the reaction container.

Although the photooxidation of aldehyde has been investigated by several research groups in recent years, the bulk of the work has been carried out at relatively high concentrations of aldehyde. Recent investigation has shown that the mechanism for the photooxidation of propionaldehyde is somewhat different at low partial pressures of aldehyde (Altshuller, Cohen, *et al.*, 1966). This type of research is significant in relation to atmospheric chemistry and suggests the need for more detailed investigations at low reactant concentrations.

Carruthers and Norrish (1936) were the first to report on the photooxidation of formaldehyde, including as products formic acid, water, carbon monoxide, carbon dioxide, hydrogen, and polymer. Later, Horner and Style, working in the millimeter range of partial pressure with formaldehyde, found hydrogen, carbon monoxide, carbon dioxide, and formic acid, but no trace of performic acid or hydrogen peroxide (Horner and Style, 1954).

Recently, Norrish and Thomas (1966) found hydrogen peroxide as a product of the thermal oxidation of gaseous formaldehyde in the millimeter range of partial pressure. With a matured quartz vessel, 70% conversion of formaldehyde to hydrogen peroxide was observed. The absence of performic acid as an intermediate in the reaction was confirmed by mass spectrometric analysis.

Experimenta

Formaldehyde, at concentrations ranging from 1 to 30 p.p.m. in air, was irradiated in reaction containers fabricated from fluorinated ethylene-propylene copolymer (FEP Teflon, Du Pont). The irradiations were carried out at $23^{\circ} \pm 1^{\circ} \text{C}$. in the same thermostated chamber used previously (Altshuller and Cohen, 1964). Mixed banks of sunlight fluorescent (wavelength maximum at 3100 A.) and blacklight fluorescent lamps (3600 A.) were ordinarily used. Formaldehyde-air mixtures in FEP containers also were subjected to solar radiation during the summer and fall months.

Concentrations of formaldehyde were determined by a modification of the chromotropic acid method (Altshuller and Cohen, 1964). Hydrogen peroxide concentrations were determined by the 8-quinolinol (Cohen and Purcell, 1967) and catalyzed-KI methods (Cohen, Purcell, *et al.*, 1967).

Results and Discussion

Previously, the photooxidation of propionaldehyde at low partial pressures had been found to give rise to a slow oxidant, which was identified by gas chromatography and kinetic colorimetry as ethyl hydroperoxide (Altshuller, Cohen, *et al.*, 1966). In a similar way, photooxidation of low partial pressures of acetaldehyde produced methyl hydroperoxide (Purcell and Cohen, 1967). The oxidant produced from the photooxidation of low partial pressures of formaldehyde probably would be hydrogen peroxide.

Colorimetry with neutral potassium iodide reagent indicates that no peroxy acid is present in the reaction vessel. This may mean that performic acid has only transient existence (Dever and Calvert, 1962), if indeed it is involved at all. On the other hand, the only identifiable oxidant produced in the photooxidation system is hydrogen peroxide. To the authors' knowledge, this is the first time hydrogen peroxide has been

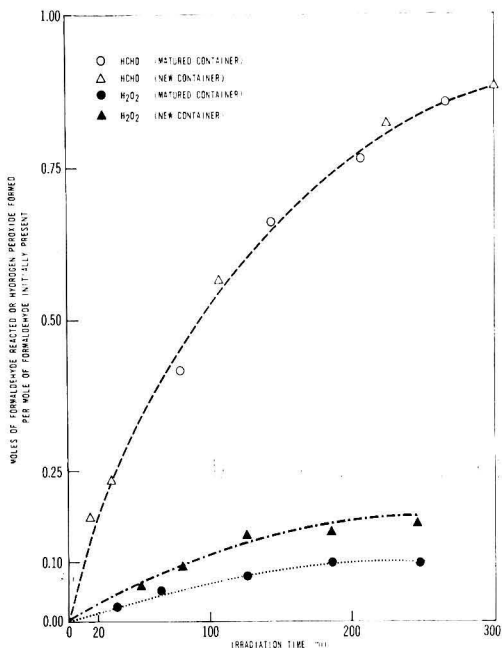


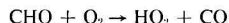
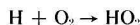
Figure 1. Relative molar yields of formaldehyde consumed and of hydrogen peroxide formed after various reaction times

reported as the oxidant produced by the photooxidation of formaldehyde.

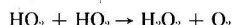
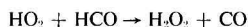
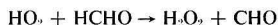
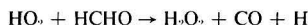
The primary process for the photolysis of formaldehyde at 3100 Å. is reported (Calvert and Steacie, 1951) as follows.



In the presence of high partial pressures of oxygen, the hydroperoxyl radical should be formed.

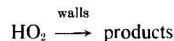


The subsequent formation of hydrogen peroxide can be explained as follows.



In the present work, a molecular balance between the aldehyde consumed and the hydrogen peroxide formed is clearly lacking, especially at longer irradiation times (Figure 1).

This apparent discrepancy might well be explained by referring to the surface reactions that reportedly occur in the thermal oxidation of formaldehyde (Horner, Style, *et al.*, 1954; Norrish and Thomas, 1966):



A new Teflon container yielded slightly higher hydrogen peroxide concentrations than were obtained with a matured Teflon bag, which had been conditioned by several gaseous photooxidation experiments (Figure 1).

These results clearly indicate that surface effects play a significant role in product formation and thus require additional investigation before a complete understanding of the mechanism for gaseous photooxidation reactions at low partial pressures of formaldehyde can be realized.

Literature Cited

- Altshuller, A. P., Cohen, I. R., *Intern. J. Air Water Pollution* **8**, 611 (1964).
 Altshuller, A. P., Cohen, I. R., Purcell, T. C., *Can. J. Chem.* **44**, 2973 (1966).
 Calvert, J. G., Steacie, E. W. R., *J. Chem. Phys.* **19**, 176 (1951).
 Carruthers, J. E., Norrish, R. G. W., *J. Chem. Soc.* **1936**, p. 1036.
 Cohen, I. R., Purcell, T. C., *Anal. Chem.* **39**, 131 (1967).
 Cohen, I. R., Purcell, T. C., Altshuller, A. P., *ENVIRON. SCI. TECHNOL.* **1**, 247 (1967).
 Dever, D. F., Calvert, J. G., *J. Am. Chem. Soc.* **84**, 1362 (1962).
 Horner, E. C. A., Style, D. W. G., *Trans. Faraday Soc.* **50**, 1197 (1954).
 Horner, E. C. A., Style, D. W. G., Summers, D., *Trans. Faraday Soc.* **50**, 1201 (1954).
 Norrish, R. G. W., Thomas, J. M., *Nature* **210**, 728, 1356 (1966).
 Purcell, T. C., Cohen, I. R., *ENVIRON. SCI. TECHNOL.* **1**, 431 (1967).

Received for review May 22, 1967. Accepted October 3, 1967.

Particle identity in fact, theory, and practice

The Particle Atlas. Walter C. McCrone, Ronald G. Draftz, and John Gustav Delly. xv + 406 pages, illus. Ann Arbor Science Publishers, Inc., Ann Arbor, Mich. 48106. 1967. \$125, hard cover. *Dr. Richard D. Cadle is head of the chemistry and microphysics department of the National Center for Atmospheric Research, Boulder, Colo. 80302.*

By *Richard D. Cadle*

Although many books have been written concerning microscopy and its application to the identification of various substances, this is the first, to my knowledge, which deals exclusively with the identification of small particles. In the Introduction the authors describe several applications of particle identification, such as the operation of clean rooms, the monitoring and control of air pollution, and criminalistics. They point out that microscopy and related techniques often provide a rapid, relatively inexpensive way to identify particles.

Scientific and technical laboratories contain many microscopes but few persons skilled in using them. In fact, many months are usually needed to learn the proper use of the microscope for identifying particles with the array of techniques often called chemical microscopy. Even so, identifications can often be made by a beginner, and his ability will improve if he makes the effort to learn.

This book is much more than an atlas. It describes in detail the skills necessary for sampling particles, manipulating them, and identifying each of the particles in a sample. The general appearance of the image of a particle as a means of identification is emphasized. The authors state that the microscopist uses the same mental processes to identify single small particles

that he uses to identify macroscopic objects, and that literally thousands of substances can be identified simply by mounting them between microscope slide and cover slip, adding a mounting liquid, and observing the image of the particle. The extent to which this approach can be applied is probably exaggerated, but it is true that the appearance of a particle is often sufficient to permit identification. Fortunately, the book describes in detail methods for obtaining additional information by microscopy which can aid in the identification. In fact, the senior author has had many years of distinguished experience in the development and application of such techniques.

The book is divided into three major parts, entitled Principles and Techniques, The Atlas, and Analytical Tables. Part One is a very detailed description of the application of microscopy to particle identification, taking a text-book approach. There are several sections or chapters and the first of these is a rather conventional discussion of optics in general, microscope optics, the parts of a microscope, and laboratory design. Much of this material is found in standard texts on microscopy, but the emphasis on proper illumination and the use of a relatively dust-free work area is especially welcome. In fact, there are obvious advantages to conducting microscopy of this type in a clean room or "clean work station." On the other hand, the statement made on page 23 that all artificial aids, from micromanipulators to mechanical stages or even stage clips, are encumbrances and should be avoided is certainly open to question. Each of these devices is at times appropriate. For example, mechanical stages are almost a necessity when the proportions of various types of particles in samples collected on microscope slides from the atmosphere are to be determined. Micromanipulators are almost indispensable for certain sit-

uations, but should only be used if absolutely necessary.

The next section deals with the collection of airborne particles. It is necessarily only a summary of this complicated subject and there is evidence that the authors are less familiar with this subject than with the others in the book. For instance, the discussion of the source of thermal forces on particles is an oversimplification. Nonetheless, the inclusion of this section greatly increases the usefulness of the book to the neophyte and the numerous references largely compensate for any inadequacy.

The third section is an excellent discussion of the preparation of samples for microscopical examination. It is often useful to fractionate the sample before studying it microscopically and various methods of fractionation are described. Separations may be based on density, size, mass, magnetic properties, solubility, and the like. These are discussed with emphasis on methods useful to the microscopist. Methods for handling particles which have been collected in various ways are included in this section and reflect many years of experience with such difficult tasks as mounting on microscope slides particles which have been collected on various types of filters. I know from personal experience the frustration that is often involved in developing such techniques.

The last section of Part One deals largely, but not entirely, with the identification of particles by their crystallographic properties. The weakest part of this section is that dealing with particle size measurement. There is no discussion of how diameters of irregular particles are defined and only one type of eyepiece graticule or micrometer is described. No mention is made of the automatic and semiautomatic methods of size determination with microscopy, nor the need to measure the sizes of many particles to obtain

Now— a true Total Organic Carbon analysis in minutes



The new Beckman Model 915 Total Organic Carbon Analyzer gives a complete TOC determination in less than 5 minutes by eliminating time-consuming sample preparation procedures. It quickly determines both total carbon and total inorganic carbon with TOC calculated by the difference.

The 915 is modular, compact, and versatile—offering analysis ranges from 0-50 up to 0-4000 milligrams organic carbon per liter of sample. Its operation follows an approved ASTM procedure for TOC, and the data obtained can be related to BOD, COD, and other criteria.

With its time-and-labor-saving features, the 915 helps you fight a better battle against water pollution. For the details, call your Beckman Process Sales Engineer. Or write for Data File PT-16-168.

Beckman

INSTRUMENTS, INC.
PROCESS INSTRUMENTS DIVISION
FULLERTON, CALIFORNIA • 92634

INTERNATIONAL SUBSIDIARIES: GENÈVE, MUNICH, GLENROTHES,
SCOTLAND, TOKYO, PARIS, CAPETOWN, LONDON, MEXICO CITY

Circle No. 22 on Readers' Service Card

statistically significant results. However, this is not an important criticism since size is usually of importance for identification only when dealing with biological materials. Other topics included in this section are the six crystal systems; color; refractive index; the use of polarized light; the determination of other physical properties such as melting point, solubility, density, and hardness; and microchemical tests. There are also brief discussions of x-ray powder diffraction, electron microscopy, the electron microprobe, the phase contrast microscope, the interference microscope, and fluorescence microscopy. The description of the use of the polarizing microscope is very thorough and the discussion of the theory and application of dispersion staining is one of the best I have seen.

Part Two is called The Atlas and is by far the most unique aspect of the book. It consists largely of 512 color photomicrographs of particles collected from the atmosphere with accompanying morphological descriptions. More than 400 samples are included. Four types of lighting were used: plane polarized light, crossed polars, slightly uncrossed polars, and top lighting. Obviously, not all types of lighting were used for all samples. The samples were selected to represent those most often found in the atmosphere, especially when contaminated. The photomicrographs are arranged under 13 headings, such as biologicals, rocks and minerals, abrasives and polishes, and miscellaneous industrial dusts. The photomicrographs are to be used as an aid in identifying particles collected from the air by direct comparison of appearance. The authors emphasize that comparisons by the microscopist with actual identified samples are preferable to comparisons with photomicrographs, but the former are often not available. The photomicrographs are of excellent quality, and while any selection of types of samples from among the thousands occurring in the atmosphere must be somewhat arbitrary, the authors have been quite successful in selecting many of those most commonly found. To aid in identification of particles, a classification system is suggested which uses either 0 or 1 to signify the presence or absence of six different characteristics. These are transparency, color (transmitted),

color (reflected), birefringence, refractive index (relative to the medium), and shape.

Part Three consists of three tables to aid in the identification. The first is actually a set of thirty tables, each covering the characteristics of a different type of particle and arranged on the basis of the classification system mentioned above. The second is a set of tables which present dispersion staining data and the third gives the specific gravity of common particles.

The book concludes with a glossary, excellent bibliography, and indices.

In general, it is well written although somewhat repetitious. Also, I find irritating the repeated use of the adjective "particulate" as a noun, when the simple word "particle" would do.

In spite of the overemphasis of the usefulness of general appearance as a means of identifying particles, this book is a major contribution to the art of particle identification. It will be especially useful to microscopists and would-be microscopists engaged in air pollution studies or in determining the nature of particles in the "natural" atmosphere. Because of its price it will probably be purchased more by libraries than by individuals.

Latest analyses for pesticide residues

Residue Reviews. Vol. 17: Residues of Pesticides and Other Foreign Chemicals in Foods and Feeds. Edited by Francis A. Gunther. vi + 184 pages. Springer-Verlag Inc., New York, N. Y. 10010. 1967. \$8.50, hard cover. *Howard A. Jones is chief of the Pesticides Branch, Division of Food Chemistry, Food and Drug Administration, Washington, D. C. 20204*

By Howard A. Jones

The latest volume in this interesting and useful series contains six articles on a wide range of subjects—from uniform tolerances within the European Common Market countries to the use of fluorescence and phosphorescence in the analysis of insecticide synergists.

In two articles, Bowman and Beroza describe research on the application of spectrophotofluorometry and spectrophotophosphorimetry to pesticide anal-

ysis. In the first they report a comprehensive study of the fluorescence and phosphorescence of methylenedioxy-phenyl compounds as the basis for methods for the determination of synergists of this class. They conclude on the basis of present experience that the fluorometric method is superior to the phosphorimetric and is also more sensitive than current colorimetric methods for such synergists.

Specific procedures are described for the analysis of certain methylenedioxy-phenyl synergists in fly sprays, rice, flour, corn meal, and paper bags. The complexity of the cleanup procedures varies but good recoveries were obtained with all of the products.

In the second article the fluorescence and phosphorescence characteristics of 17 insecticidal carbamates were studied as a basis for development of an analytical technique for residues. In general these characteristics do not appear very useful for the purpose. Only five of the carbamates showed sufficient emission intensities for development of an analytical procedure. The authors describe such a procedure applicable to analysis of milk. Although recovery values and precision are adequate, the sensitivity is relatively poor.

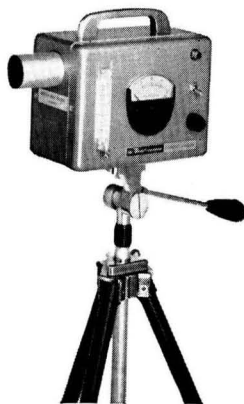
Residue screening

Samuel and Hodges review screening methods for insecticide residues. The authors cover several popular multiresidue methods, arranged so that sample preparation, extraction, cleanup, and determination are discussed separately. This arrangement permits the assembly of a total method comprised of techniques from different authors. Advantages and disadvantages of various techniques and procedures are pointed out.

The section on extraction is somewhat disappointing: possibilities of incomplete extraction and the lack of research on completeness of extraction of weathered residues are not strongly emphasized. The extensive bibliography extends to early 1966.

International standards

A brief discussion by Dormal describes efforts to adopt uniform pesticide residue tolerances and analytical methods within the European Economic Community. It is gratifying to



**This air sampler
does everything
you'd expect.
Except choke up.**

It can't choke up or clog—it doesn't have a filter. Dusts, fumes, smokes, bacteria, oil mists and other aerosols are collected *electrostatically*. At rates from 3 to 8 cfm and efficiencies of 98-99% without *any* drop in air flow.

The Bendix® Electrostatic Air Sampler Kit—complete with solid state power supply, rechargeable battery, tripod, cables, extra probe wires and spare collector tubes in a rugged luggage case—makes field setups a snap. With no filter action to overcome, it doesn't need a heavy pump. That keeps the whole kit down to a trim 27 pounds in the 17" x 16" x 7½" vinyl-covered case. And it works on AC, too.

Bendix scientific instruments—including mass spectrometers, atomic absorption and flame spectrophotometers, polarimeters, polarographic systems and electron multipliers—are used in over 100 areas of research and analysis. For more information, write: **The Bendix Corporation, Scientific Instruments Division, 3625 Hauck Road, Cincinnati, Ohio 45241. Or phone (513) 772-1600.**



Circle No. 37 on Readers' Service Card

know that international cooperation is leading to progress in these matters.

Gunther, Buzzetti, and Westlake describe a timely and useful study on the behavior of polynuclear hydrocarbon residues on oranges. The methodology employed to isolate and determine the hydrocarbons from the fruit appears to be sound as evidenced by reported recovery values. One feels some apprehension, however, about the proposed procedures for correction of fluorescence observations for impurities in solvents. Although the authors state that the validity of such corrections must always be critically questioned and justified, the use of impure solvents for fluorescence studies should be discouraged particularly when adequate purification is attainable. The proposed "anthracene index" as a possible general guide to the probability of polynuclear contamination of foodstuffs is of doubtful value. There is evidence in the literature to indicate that higher

polynuclear compounds, including carcinogens, occur even when anthracene is absent, or present in relatively insignificant proportions.

Metabolism in grains

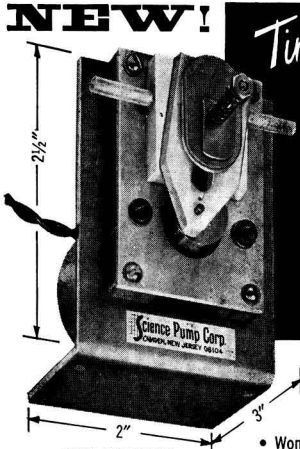
Rowlands has contributed a most comprehensive survey of the subject of metabolism of insecticides in stored grains, much of the material being derived from the author's own research. The review also covers such related information as physical and biological changes in grain during storage and penetration of insecticides into grain. Since the pathways by which insecticides are metabolized in stored cereal grains are not well known, the author also includes in satisfactory detail a review of degradation reactions and rates in other plant tissues, and alterations caused by microorganisms. The interesting stepwise degradation of some organophosphorus insecticides in stored grain is discussed.

Observations

I feel that Rowlands has not cautioned sufficiently against the use in stored edible grain of some of the more toxic and persistent insecticides (like the cyclodienes) which he discusses. Also, he gives the impression that DDT may be used on stored cereal grains, but as Table I shows, there is no tolerance which would allow the use of DDT on stored grains in this country. One must agree with the author's hope "that data on the metabolic fate of insecticides in stored grain will ultimately be a standard legislative requirement for any insecticidal compound intended for application to stored food products." The bibliography is quite extensive.

As in previous volumes, there are items in the present volume which will be of value to the inexperienced residue chemist as well as to the worker who has spent some time in this interesting field.

NEW!



Tiny **GAS SAMPLING PUMP**

MADE OF TEFLON*
...is non-reactive,
non-contaminating

Patented by W. D. Komhyr
U.S. Patent No. 2,242,689

Pump with motor weighs only 5 1/2 ounces

FEATURES

- Won't contaminate or destroy chemically active gases because gas-contacting parts are Teflon® reinforced with 15% glass fiber and no lubrication is required.
- Pumps inert gases without contaminating them.
- Offers approx. 200 ml/min. flow rate (non-adjustable). Flow rate is constant within ±1.5% of mean value.
- Develops pressure or suction equivalent to a 3-inch column of mercury in normal operation.
- Performs dependably at atmospheric pressures from sea level to 2 mbs.
- Is operated by a 6V d.c. motor having a governed speed of 2400 r.p.m.

*Du Pont Reg. T.M.

APPLICATIONS

Air Pollution Studies
Ozone Measuring Devices
(Pump will not destroy ozone!)

Trace Gas Measurement
Lab Gas Analyses

Write for
FREE
Descriptive
Bulletin

Science Pump Corporation

1431 Ferry Avenue, Camden, N. J. 08104
Phone: (609) 963-7700

Circle No. 17 on Readers' Service Card

Exchange of ideas on fresh water

The Fresh Water of New York State: Its Conservation and Use. Edited by Lauren B. Hitchcock. A symposium. xviii + 255 pages. William C. Brown Book Co., Inc., Dubuque, Iowa 52001. 1967. \$5.00, hard cover. *William C. Ackermann is chief, Illinois State Water Survey.*

By William C. Ackermann

This book is the proceedings of a symposium held at the State University of New York at Buffalo (June 13-17, 1966). It was conducted by the School of Engineering of that University and co-sponsored by the Buffalo Section of the American Society of Civil Engineers.

The purposes and policies of the symposium were to provide for the exchange of ideas and for discussion among professionals. However, there is much of value for the informed and interested lay person. Some 65 prominent speakers identified and discussed the major water problems confronting the people of New York in conserving and extending their abundant water

resources. Goals were defined and the technology required to achieve these goals was identified.

The quality of the symposium and the book are a direct function of the star-studded list of participants. These included political leaders Governor Nelson A. Rockefeller and Senator Edmund S. Muskie whose effective leadership lends conviction to their remarks. New York State has a first-rate team of water professionals who spoke—men like Harold G. Wilm, F. W. Montanari, Leonard Dworsky, and others. The federal agencies were represented by men like Leon Weinberger, Eugene W. Weber, Roy T. Dodge, and Murray Stein. Consultants were represented by Richard Hazen and George O. G. Löf. Since discussion involved the international waters of the Great Lakes it was appropriate that Canadians Robert H. Clark, Thomas W. Kierans, and others were present to present papers.

While the symposium was directed primarily to the problems of New York State, much of what was said applies elsewhere.

Major recognition was given to using water to meet the needs of man. The resource available was summarized along with the major problems and the manpower, financial, technical, and political steps which must be taken to bring solutions.

Despite the intention that the symposium is by and for professionals, this reviewer feels that since the papers and discussions are not highly technical, they are really most useful to the administrator, legislator, industrialist, and interested citizen who need a balanced picture.

Perhaps this was summarized by one of the speakers, Professor Ross E. McKinney, who said: "So much has been written and so much has been said about water resources management that one cannot help but wonder if there is anything meaningful left to say. The problem we face is a simple one, but its solution is far from being simple. The reason for this lies in the fact that like most problems there is no one solution, but rather there are a number of possible solutions. Each one of these solutions has its advantages and its disadvantages as well as its proponents and its opponents."

What's new in waste water treatment systems?



NEW BOWSER-BRIGGS "GRAVI-PAK"

OIL/WATER SEPARATOR FOR
FREE UNEMULSIFIED OIL REMOVAL



NEW BOWSER-BRIGGS "GRAVI-FLOTE"

COMPLETE PACKAGED TREATING
SYSTEMS FOR POLLUTION CONTROL

Get all the facts in these two
new product bulletins. Mail coupon
for your free copies today!



BOWSER-BRIGGS FILTRATION DIVISION
COOKEVILLE, TENNESSEE 38501

IN CANADA: S. F. BOWSER CO., LTD., HAMILTON, ONTARIO

EST-3

Write for what's new in waste water treatment systems. Ask for Gravi-Pak bulletin C69-65 and Gravi-Flote bulletin C70-65.

Name

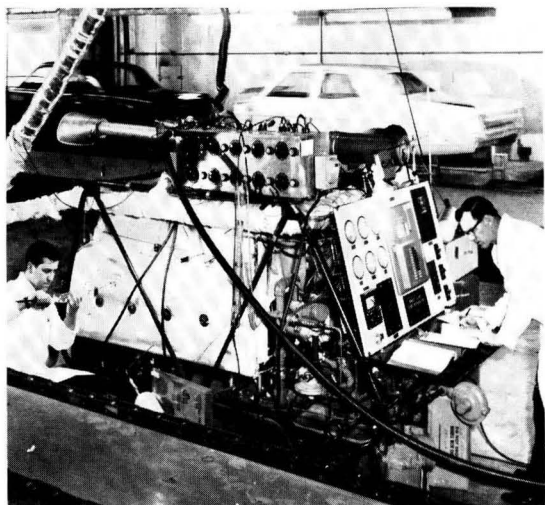
Company

Address

City State Zip

Circle No. 14 on Readers' Service Card

NEW PRODUCTS DIGEST



A portable fume incinerator was used to help arrive at parameters for control of solvent emissions from auto paint bake ovens at Ford Motor Co.'s Los Angeles assembly plant. The unit determined how effectively direct-flame incineration eliminates fumes from the bake ovens. Incorporated in the incinerator is a recuperative heat exchanger, which permits the system to recover heat generated by incineration and so reduce fuel requirements. Air Preheater Co., Inc.

61

Ion Electrode Standards

Nine standard solutions for specific ion electrodes are available. They are for use with the Ionalyzer specific ion electrodes used for water hardness, calcium, nitrate, fluoride, chloride, bromide, and iodide. Orion Research, Inc.

62

Flowable Materials Pump

Elastacurv pump handles all flowable material even when the liquids contain foreign matter such as slurries, sand, and metal particles. The pump requires no lubrication; all rotating parts are mounted on permanently lubricated bearings. Available are models with speed ranges from 50 to 4000 r.p.m., a variety of outputs in g.p.m., and pressure ranges from 0 to 1000 p.s.i. Mercury Electronics Corp.

63

Asphalt Plant Dust Collector

Specifically designed for asphalt plants, Model UDT dust collector keeps stacks consistently free of discharge. The equipment can collect as much as 10,000 pounds of aggregate per hour. The collector, already in operation at Mayer Paving & Asphalt (Skokie, Ill.), uses Nomex needle-felted filters, which can be used at operating temperatures to 425° F. Flex-Kleen Corp.

64

Environmental Chambers

The Agree chambers can be used to handle temperature and vibration tests established by the Advisory Group of Reliability of Electronic Equipment (AGREE). The units have a working temperature range of -125° to 300° F. and can be fitted with a vibrator diaphragm. Webber Manufacturing Co., Inc.

65

ATLAS ANALYZERS and CONTROLLERS

for



AND TOTAL OXIDANTS



AND OTHER REDUCING AGENTS

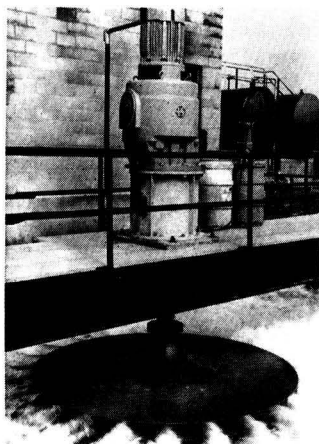


Gas Detector Kit

A portable kit for determining trace concentrations of 70 toxic gases and vapors is available. The kit contains a precision pump, accessory parts, and 6 boxes of detector tubes. Test reagents, contained in special, sealed chemical detector tubes, are ready for use without prior mixing. Union Industrial Equipment Corp. 66

Surface Aerator

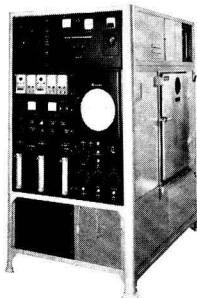
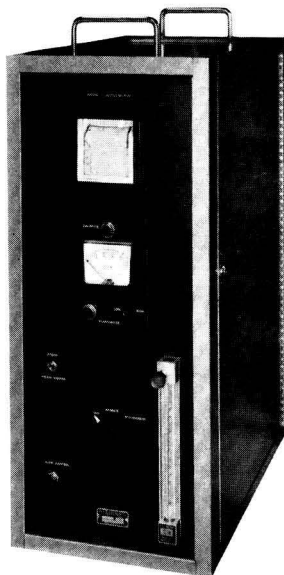
The Turborator Aerator is suitable for the treatment of both industrial and domestic waste waters. Because of special impeller vane construction and air intake ports, it provides from 4.5 to 5.5 pounds of oxygen per output shaft horsepower. The unit is built of corrosion resistant polyester reinforced laminated material and is available in sizes from 10 inches to 10 feet in diameter. It is corrosion resistant in a pH range of 2 to 12 and, thus, is adaptable to industrial treatment of highly corrosive waste waters. FMC Corp. 67



for use wherever specific concentrations of gases are to be measured or controlled.

- New Schulze Method of Analysis
(Patent applied for)
- Accurate analysis with high sensitivity
- Variations of 0.001 ppm/v can be detected
- Extremely fast response
- Built-in electronic calibration
 - Continuous recording
- Unattended weekly operation
 - Shipped complete, ready to operate

Write for complete technical information



ATLAS 600 Series

Weather-Ometer® and test chamber

Atmospheric contaminants can be controlled automatically in combination with temperature and humidity with or without simulated sunlight. Basic models available with variations of controls.

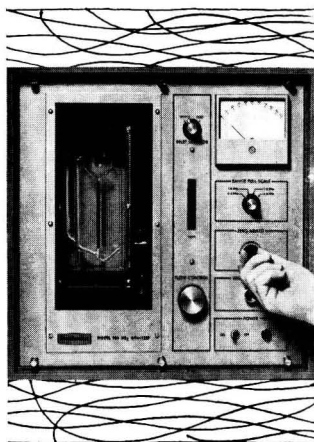
For over 40 years manufacturers of testing machines for Weathering and Fading.

ATLAS ELECTRIC DEVICES COMPANY

4114 N. Ravenswood Ave.
Chicago, Illinois U.S.A. 60613
Phone: 312-327-4520

Circle No. 28 on Readers' Service Card

Specific, simple SO₂ monitoring from Beckman.



With the new Beckman Model 906 SO₂ Analyzer, you don't have to worry about reagents. Or metering pumps. Or fragile glass contactors. Or complex external sample handling systems. Or many other complex components. Or the high maintenance costs usually entailed.

By incorporating the technique of secondary coulometry with a unique end-point detector, and a patented scrubber, which virtually eliminates all interference errors, the analyzer provides rapid, **continuous**, accurate and specific determinations of SO₂ concentrations in ambient air.

SPECIFIC FEATURES. 1. Response time is less than 3 minutes. 2. Zero calibration built in. 3. Panel, wall or bench mountable. 4. Four operating ranges from 0.5 to 4.0 ppm full scale; switch selectable. 5. Linear direct readout, recorder output. Call your Beckman office or write for Data File AP-16-267.

Beckman

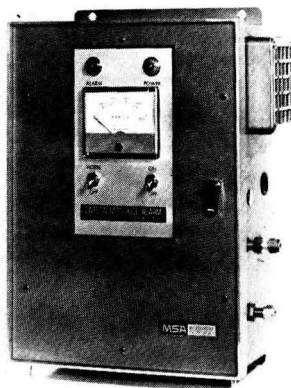
INSTRUMENTS, INC.

PROCESS INSTRUMENTS DIVISION

FULLERTON, CALIFORNIA • 92634

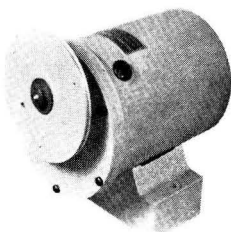
INTERNATIONAL SUBSIDIARIES: GENEVA, MUNICH, GLENROTHES, SCOTLAND, TOKYO, PARIS, CAPE TOWN, LONDON, MEXICO CITY

Circle No. 26 on Readers' Service Card



CO Analyzer-Alarm

Model 701 analyzer uses a catalytic oxidation principle and features solid state circuitry. It gives both visible and audible warning of CO concentration at preset levels in the range of 0 to 500 p.p.m. Mine Safety Appliances Co. **68**



Position Motor Telemeter

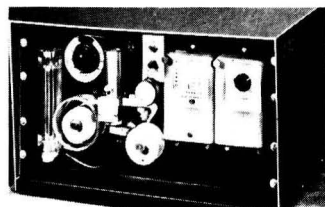
Type P transmitter, one of several units available, registers the position of any moving element at a distant (to 3 to 4 miles) location. Moving elements such as water level, gate position, and the like cause the transmitter shaft to turn a motor rotor similar to the motor rotor that follows the motion exactly at the receiver. Leupold & Stevens Instruments, Inc. **69**

Temperature Test Chamber

The Tenney, Jr., bench-type high-low temperature test chamber has solid state instrumentation with automatic reset capability. The chamber has a working temperature range of -120° to +350° F., with a $\pm 1/4^\circ$ F. control throughout the range. Tenney Engineering, Inc. **70**

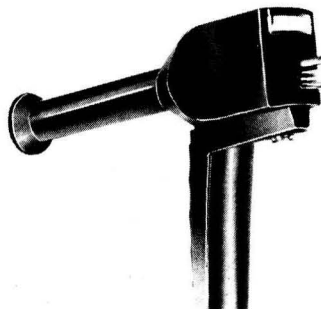
High Volume Air Sampler

Model 8000 is a high volume sampler capable of continuous operation for as long as 1000 hours. The model features a flowmeter that is physically separated from the motor cooling air, thus preventing carbon brush particles from entering. The device is portable and is designed so that motor brushes can be replaced easily. Electro-Neutronics, Inc. **71**



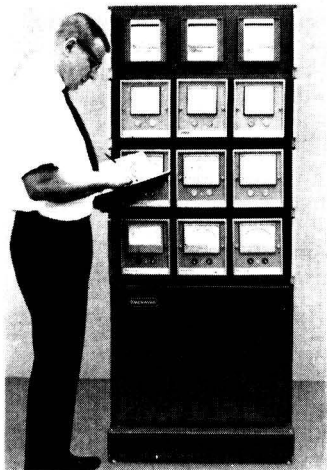
Air Sampler and Analyzer

The Sentinel Phototape Sampler-Recorder can be used in the collection and evaluation of air samples in H₂S studies, industrial air pollution control, studies of plant environments and community air pollution. The recorder, which provides for adjustable sampling time control, also gives a 30-day permanent record of relative contamination levels. An audible or visual alarm for the system is available. Gelman Instrument Co. **72**



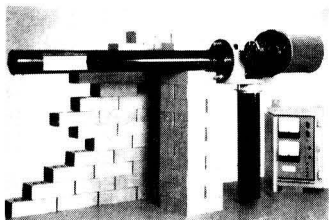
Leak Detection Probe

The meter probe can be used to detect pinhole leaks in filter systems and, thus, is especially suited for clean and white room applications. The probe's meter indicates the magnitude of the leak. Phoenix Precision Instrument Co. **73**



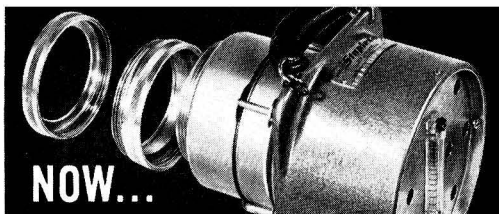
Water Quality Monitor

Model 9500 water quality monitor can be used to make 24-hour measurements of a wide range of eight water pollution variables, including pH, chloride ion concentration, oxidation-reduction potential, conductivity, dissolved oxygen, temperature, turbidity, and solar radiation intensity. All, or any combination of these variables, can be monitored with this unit. The monitor can be placed in an on-shore shelter, with water samples being continuously drawn from a nearby stream or lake by a submersible pump. Beckman Instruments, Inc. **74**



In-Stack SO₂ Monitor

The SO₂ monitor can be fitted directly into a breeching to record, continuously, SO₂ at the p.p.m. level in flue gases. It requires neither chemicals, water, nor the services of a skilled technician. The monitor uses an optical correlation technique, and operates in the u.v. region of the spectrum. Its accuracy ($\pm 5\%$ full scale) is unaffected by the temperature of the flue gas. Barringer Research, Ltd. **75**



NOW...

SAMPLE AIR FASTER, MORE ACCURATELY, PORTABLY

Accurate to
1/100 micron!

INDISPENSABLE for series or unit air sampling — indoors or out. Portable, yet stands up to heaviest usage. Weighs only 10 lbs. Comes equipped with standard 4" filter holder. Special adapters available for 6" x 9"; 8" x 10"; 12" x 12" and others.

Staplex Air Samplers are widely used to solve the many diverse, exacting needs of leading industries. Also for industrial hygiene and health departments, nuclear and missile fields; manufacture and processing of beryllium products, radioactive materials and all other industrial dusts and air pollutants.

Let us help you solve your air sampling problems as we have for thousands of users. Send for details.

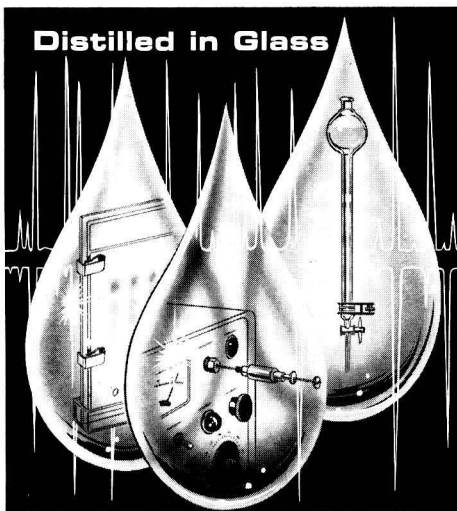
THE *Staplex* COMPANY AIR SAMPLER DIVISION

783 FIFTH AVENUE • BROOKLYN, NEW YORK 11232

World's Largest Manufacturer of High Volume Air Samplers

Also available new line of Low Volume and Self-Charging Battery Air Samplers.

Circle No. 20 on Readers' Service Card



Distilled in Glass

...to meet exacting solvent needs

Acetone • Acetonitrile • Benzene • Butanol-1 • Butanol-2 • Carbon Tetrachloride • Chloroform • Cyclohexane • Dimethyl Formamide • Dimethyl Sulfoxide • Dioxane • Ethyl Acetate • Ethyl Ether • "Heptane", 95-99° • Hexane, 68-69° • Methanol • 2-Methoxyethanol • Methylene Chloride • N-Methylpyrrolidone • Pentane • Petroleum Ether, 30-60° • Propanol-2 • Tetrahydrofuran • Toluene • Trimethylpentane • Others...

Ask for Bulletin BJ-13K U.S. Agencies use F.S.S.

BURDICK
& JACKSON
LABORATORIES, INC.

616 722-2310 OR 722-7480

MUSKOGON, MICHIGAN 49442

Circle No. 27 on Readers' Service Card

Submicron Aerosol Analyzer

Model 3000 aerosol analyzer can be used to size and count airborne particles in the range of 0.015 to 1.0 micron diameter. The unit can be programmed for automatic or remote operation and is useful for studies on air pollution, tobacco smoke, radioactive aerosols, combustion aerosols, electric charge on aerosols, lung retention, laboratory aerosols, and the like. Thermo-Systems, Inc. 76

NonChromate Corrosion Inhibitor

Dearborn 909 inhibits corrosion in open cooling towers and airwash systems. This inhibitor contains no chromate and is based on a combination of organic heterocyclic compounds, a zinc salt, an organic sequestrant, and an alkalinity stabilizing agent. The

inhibitor can also be used to reduce scaling and fouling on heat transfer surfaces and is effective over a pH range of 6.5 to 8.0. W. R. Grace & Co. 77

Automatic DTA Apparatus

Model TA-L differential thermal analyzer can be used to measure the thermal changes of a sample and a standard and record both simultaneously by means of a strip chart recorder. The analyzer can be used for thermal analysis; rates of reaction; heats of absorption, adsorption, and desorption; and the like. Voland Corp. 78

Sludge Pumps

Sludgemaster pumps handle concentrated solids in a sewage treatment

plant. Two standard types of this pump are available—simplex and duplex. The pumps feature a cylindrical sleeve-type piston guide and gland, polyurethane checkballs, replaceable cast bronze valve seats, and high tensile iron cylinders. Multipiston units are available upon special request. Dorr-Oliver, Inc. 79

Portable Oven for Field Use

Portable Hi-Way oven meets ASTM specification for vented, forced-draft ovens. Designed to dry soil and aggregate samples, the oven features radiant hotwall heating that is thermostatically controlled from ambient to 390° F. The unit is of double-wall construction and equipped with handles for portability in the field. Lab-Line Instruments, Inc. 80



FOR LABORATORY OR IN THE FIELD —
IT ALWAYS PAYS TO SPECIFY
THE DEPENDABLE AND ORIGINAL . . .

Drummond MICROCAPS®

(DISPOSABLE MICRO-PIPETTES)

GUARANTEED ACCURACY TO ONE PERCENT

AVAILABLE IN 37 STANDARD SIZES —
FROM ONE HALF TO 100 LAMBDA S

SPECIAL SIZES MADE TO YOUR ORDER

EASIEST MICRO-PIPETTE TO USE —
NO NEED TO FILL TO A LINE

ECONOMICAL ENOUGH TO USE ONCE AND DISCARD

Send for free samples and complete descriptive literature

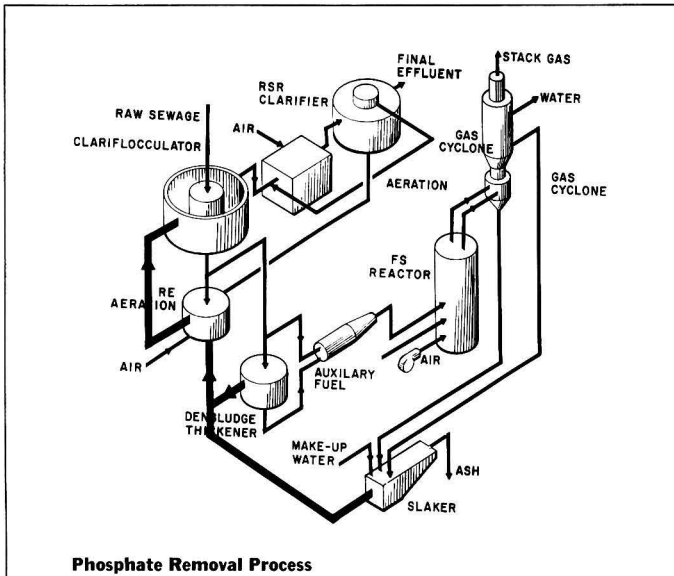


Made in U.S.A. by
Drummond Scientific Company

500 PARKWAY • BROOMALL • PENNSYLVANIA • 19008

Circle No. 32 on Readers' Service Card

NEW LITERATURE DIGEST



Phosphate Removal Process

Elimination of the need for tertiary treatment is the claim Dorr-Oliver, Inc., makes for its PEP system for removing phosphate from municipal wastes. PEP (Phosphate Extraction Process) works this way: Lime is added to the primary settling tank, removing 85% of the suspended solids and 65-75% of the raw biological oxygen demand. Phosphate levels drop from a typical 20 to 30 mg. per liter to 3 to 6 mg. The remaining phosphate is removed in the secondary or biological treatment step. Most approaches to phosphate removal involve a tertiary step—addition of a chemical to precipitate phosphate from the secondary effluent. Dorr-Oliver claims that PEP:

- Reduces chemical cost by 60-70%.
- Reduces sludge handling cost by 50%.
- Requires no recarbonation step.
- Reduces cost of secondary treatment by 50%.
- Reduces operational cost of phosphorus removal.

Circle 81

Fight for clean air. A 6-page reprint from the June, 1967 *AFL-CIO American Federationist* summarizes federal activities relating to the problem and restates the union's position and planned actions. It is also a review of the growing need for air pollution control. AFL-CIO. **82**

Urban environmental problems. Volume XXI, No. 6, of *Engineering Progress* contains six selected papers presented last year at a graduate seminar at the University of Florida Water Resources Research Center. The topics include economic aspects of water quality, the role of the Federal Government, planning and the urban environment, recreation uses of land and water (also associated bioenvironmental problems), an agricultural economist's view of research in environmental engineering, and the economics of environmental engineering. University of Florida. **83**

Dust collector. A 12-page bulletin, PC-2, describes Mikro-Pulsaire units for dust recovery and dust control. The dry filter collector, which can handle dust streams with temperatures as high as 425° F., is automatic, self-cleaning and has no internal moving parts. All controls are on the outside of the units. Slick Industrial Co. **84**

Corrosion inhibition. Bulletins CB-101 and CB-102 describe coating products formulated to prevent corrosion on metal surfaces. The products, Lube-Coat and DryCoat, offer transparent coatings and permit rapid surface evaluation, easy application, and removal. Tracor, Inc. **85**

Aerosol, dust, and smoke photometer. An 8-page bulletin, JM-2000 A, describes a photometer that can be used for measuring the dust load (mass concentration) of particulate matter in the atmosphere. The actual value of the mass concentration corresponding to a reading of the instrument depends on the type of particulate matter in the atmosphere—particle size, shape, refractive index, and color. The instrument must be calibrated by the user with an aerosol of known particle size and physical properties. Cenco Instruments Corp. **86**

Organic fluorine compounds. Catalog F-16 is a 36-page handbook of organic fluorine compounds supplied by the company. In addition, the catalog contains a special section on inert fluids for coolant, lubricant, and heat transfer media, and other applications demanding unusual stability under extraordinary environmental conditions. Pierce Chemical Co. **87**

Chemical catalog. A new catalog lists more than 6000 reagent and organic chemicals. Included, also, is a section on safety, how to handle toxic and hazardous chemicals, their flammability, and what to do in case of accident. Ace Scientific Supply Co., Inc. **88**

Gas sampling pump. A 4-page bulletin describes a small, nonreactive, Komhyr Teflon pump that can be used with ozone measuring devices and in trace gas and air pollution measurement. The pump requires no lubrication and has a pumping capacity of 200 ml. per minute. Science Pump Corp. **89**

Air and water quality measurement. Bulletin I 100 describes data gathering systems for concurrent monitoring of both air and water pollutant concentrations. The bulletin includes a description of systems for on-site recording, analog telemetering, and digital telemetering. Bristol Co. **90**

Ozone in water treatment. A 4-page brochure discusses the use of ozone as a disinfectant and oxidant in the treatment of drinking water. Welsbach Corp. **91**

Chloride determination. A 4-page data sheet describes how the company's Ionalyzer chloride ion activity electrode can be used in the measurement of chloride ion in the presence of oxidizing agents. The stable chloride sensor does not respond to cations and can be used in the presence of bromide, iodide, cyanide, sulfide, or ammonium ions. Orion Research, Inc. **92**

Environmental equipment. A 4-page bulletin describes humidity cabinets, temperature-humidity test chambers, laboratory ovens, a line of 90 environmental rooms, refrigerated CO₂ incubators, furnaces, and growth chambers. Hotpack Corp. **93**

Industrial water analysis. A 20-page booklet discusses sampling procedures and specific methods of analysis for total hardness, calcium and magnesium, alkalinity, hydrate alkalinity, chloride, pH, orthophosphate, sulfite, soluble silica, chromate, and others. Drew Chemical Co. **94**

Chlorination control. Bulletin R90-49-31 describes a closed loop system for the economical and efficient chlorination of raw or treated water and sewage effluent. Improved instrumentation permits continuous control and analysis of residual chlorine. Fischer & Porter Co. **95**

Water purification equipment. Bulletin 101 describes 33 items including aerators, clarifiers, filters, filtering units, and components. Lakeside Engineering Corp. **96**

Microorganism control. Bulletin C-208 describes Nalco 208, a bithiocyanate blend in pellet form designed to prevent microbial deposits and minimize mixed microbial-inorganic deposits. The chemical is useful in industrial recirculating water systems and can be fed on a continuous, semislug, or slug basis, depending on system characteristics. The pellets are available in 100 pound drums. Nalco Chemical Co. **97**

Ultrasonic transducer units. A 4-page technical bulletin sets forth a line of self-contained immersible transducers and transducerized plates powered by matching all-solid-state ultrasonic

generators. The bulletin explains the conversion of ordinary tanks and vats into ultrasonic cleaning or processing machines. Acoustica Associates, Inc. **98**

Filter chambers. Bulletin 403 describes the two tube twin filter chamber Model 10 × 2. The all plastic unit offers a choice of two bases, which permits filtration or solution purification in one instance in series, in the other in parallel. The series base arrangement has a capacity of 50-75 g.p.h.; the parallel base arrangement has a capacity of 200-300 g.p.h. The unit, which can use activated carbon or ion exchange resins, is corrosion resistant to most acid and alkaline solutions and has no metal contacts. The dual chamber device can be used in the continuous filtration of nickel, silver, and gold solutions. Sethco Manufacturing Corp. **99**

Flowmeter. An 8-page leaflet gives specifications for an in-stream flowmeter for Parshall flumes and rectangular and triangular notch weirs. A typical system arrangement and several methods of installation of the float-actuated meters are included. Fischer & Porter Co. **100**

Water quality monitoring. A 4-page folder outlines the company's water quality monitoring systems capability. Equipment for data acquisition, logging, transmission, display, and conversion are described. Models are available for automatic, continuous scanning of more than 20 physical and chemical parameters in shelter, trailer, or survey boat applications. The equipment comes in a single console or modularized design. Fairchild Space and Defense Systems **101**

Elemental analyzer. A brochure describes an instrument that analyzes organic compounds for carbon, hydrogen, nitrogen, and oxygen. The principles of operation and operating controls of the elemental analyzer are discussed. Perkin-Elmer Corp. **102**

Industrial plant equipment. The company's line of equipment designed for industry is described in a 6-page bulletin. Equipment for air moving, air heating, air pollution control, and variable speed control are included. American-Standard **103**

MEETING GUIDE

November 6-7 Oklahoma State University

18th Oklahoma Industrial Wastes and Pollution Control Conference

Oklahoma State University, Stillwater

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

November 6-8 American Water Resources Association

National Symposium on Ground Water Hydrology

Mark Hopkins Hotel, San Francisco, Calif.

The symposium will include sessions on occurrence of ground water in different geologic environments; ground water movement and well hydraulics; sea water intrusion, artificial recharge, and surface water-ground water relationships; and model and radioisotope techniques in ground water resources investigations.

November 8-10 American Water Resources Association

3rd Annual American Water Resources Conference

Mark Hopkins Hotel, San Francisco, Calif.

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

November 10 Association for Computing Machinery

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

Hilton Hotel, New York, N.Y.

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

November 13-15 University of Delaware

1st Annual Mid-Atlantic Industrial Waste Conference

University of Delaware, Newark.

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

November 14-16 American Society for Testing and Materials

Committee D-22 on Methods of Atmospheric Sampling and Analysis

ASTM headquarters and Sheraton Hotel, Philadelphia, Pa.

This year's meeting features a seminar on air quality standards, air quality criteria, and standard means for the evaluation of air quality.

November 20-22 Saul Gordon Associates

Workshop on Noise—Its Measurement and Control

Hoppatcong, N.J.

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

November 26-30 American Institute of Chemical Engineers

60th Annual Meeting

Hilton Hotel, New York, N.Y.

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

November 27-30 Entomological Society of America

1967 Annual Meeting

Hotel New Yorker, New York, N.Y.

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

November 27-December 1 International Exposition Company

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

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

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

Seminars on Water Pollution Control for Chemical Wastes

University of Texas, Austin

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

December 26-31 American Association for the Advancement of Science

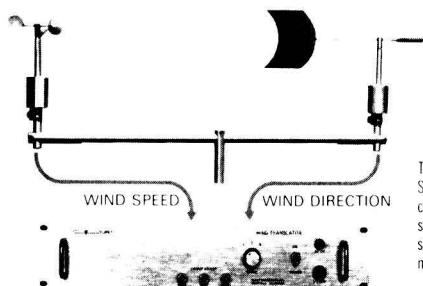
134th Annual Meeting

Americana and Hilton Hotels, New York, N.Y.

This meeting will include a general lecture (Friday, Dec. 29) on environmental pollution by Abel Wolman and a symposium (Saturday, Dec. 30) on weather modifications in arid areas.

CLIMET AIR POLLUTION DATA SYSTEM

MEASURE AND RECORD WIND FLOW AND WIND DIRECTION



This typical CLIMET Air Pollution Data System measures, computes and records wind flow and diffusion. The system is composed of the "off-the-shelf" CLIMET Meteorological Instrument Building Blocks described below.

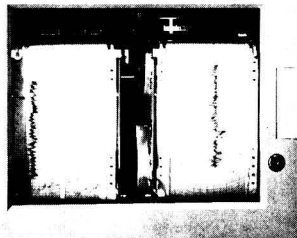
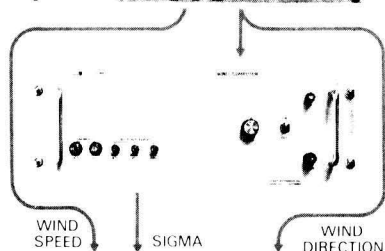
Model 011-2 WIND SPEED TRANSMITTER... A rugged 0-100 mph anemometer with a threshold of 1.5 mph and an accuracy of $\pm 2\%$ or 0.25 mph.

Model 012-6 WIND DIRECTION TRANSMITTER... A unique 540° wind direction sensor with an accuracy of $\pm 5^\circ$.

Model 026-2 TRANSLATOR... A reliable all-silicon solid state signal processor.

Model 030-5 SIGMA (Variance) COMPUTER... Electronically computes the average directional deviation of wind flow from the output signals of the wind direction transmitter.

Model 014-94 STRIP CHART RECORDER... Continuously records wind speed, wind direction, and average directional deviation. The Model 014-94 will capture more than two weeks of data on a single set of strip charts.



WRITE OR PHONE FOR YOUR COPY OF "METEOROLOGICAL INSTRUMENTATION FOR AIR POLLUTION STUDIES."

CLIMET INSTRUMENTS INC.

1240 Birchwood Drive • Sunnyvale, California 94086 • Telephone 736-6950 (408)

Circle No. 31 on Readers' Service Card

MEETING GUIDE continued

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

Symposium on Developments in Petroleum Environmental Chemistry

San Francisco, Calif.

Jointly sponsored by the Divisions of Petroleum Chemistry and Water, Air and Waste Chemistry, the theme of the symposium will include the chemical characterization and chemical control of aqueous and gaseous wastes from the production, refining, distribution, and use of petroleum products.

April 3-5, 1968 Pollution Control Exposition and Conference

Astrohall, Houston, Tex.

Sponsored by the Houston Junior Chamber of Commerce, the exposition is aimed at potential users of pollution control equipment and will feature exhibits of equipment for all kinds of pollution—air, water, noise, and solid waste. The associated conference will encompass the latest in technical reports from all of the industries concerned with the control of pollution in our environment. One feature of the sessions is a planned panel discussion concerning the role of the Federal Government in pollution control.

CALL FOR PAPERS

May 21-23, 1968 American Meteorological Society

8th National Conference on Agricultural Meteorology

Carleton University, Ottawa, Canada

Papers are solicited on aspects of agricultural and forest meteorology such as weather information applied to decision making, micrometeorological studies of crops and forests, interactions between organisms and their environment, photosynthesis and water-use efficiency, and environmental manipulations and control. Abstracts should be sent to Dr. K. M. King, University of Guelph, Ontario, Canada, before December 1. The meeting will also feature a special session on the International Biological Program.

July 22-24, 1968 American Medical Association

9th Air Pollution Medical Research Conference

Denver, Colo.

Papers dealing with epidemiology, respiratory biochemistry and physiology, including clearance mechanisms and experimental models, immunology and hypersensitivity, experimental pathology, and controlled studies of therapeutic applications, particularly in humans are solicited for presentation at this conference. Abstracts (two copies) of 250 words or less should be sent to Dr. Gordon R. Engebretson, American Medical Association, Department of Environmental Health, 535 North Dearborn St., Chicago, Ill. 60610.


PROFESSIONAL CONSULTING SERVICES

JOHN J. BAFFA
Consulting Engineers
John J. Baffa Nicholas J. Bartilucci
 Industrial Waste Treatment
 Sewers & Sewage Treatment
 Water Supply & Treatment
 Refuse Disposal, Drainage & Flood Control
110 Washington St., New York, N. Y. 10006

BETZ
 THE VOSE, PENNSYLVANIA 19047
 CONSULTING SERVICES DIVISION
 Air Pollution • Process Water • Industrial Wastes
 Analyses Design
 Evaluations Specifications
 Treatability and Reuse Studies

ENGINEERING-SCIENCE, INC.
 Environmental Engineering
 Consulting and Research
**150 E. Foothill Blvd.
 Arcadia, California 91006**

REGISTERED PROFESSIONAL ENGINEER AIR POLLUTION CONTROL
 CALIFORNIA NEW YORK
CARL R. FLODIN
 CONSULTING ENGINEER
 682-1800 2744 MONTEREY ROAD
 AREA CODE 213 SAN MARINO, CALIF. 91108

 **CYRUS WM. RICE** AND COMPANY 15 Noble Avenue, Pittsburgh, Pennsylvania 412-921-6000
WATER MANAGEMENT CONSULTANTS
 Economics of Water Resources
 Instrument Development Water Systems Analysts
 Water Reuse and Quality Control
 Material Evaluations Corrosion Studies
 Information Retrieval & Data Handling Systems
 Waste Water Treatment
**COMPLETE ENGINEERING AND
 LABORATORY SERVICES**

DAMES & MOORE
CONSULTING ENGINEERS IN APPLIED EARTH SCIENCES
 Air Pollution Water Pollution
 Solid and Liquid Waste Disposal
 Environmental Studies For Nuclear Power Plants
100 CHURCH STREET, NEW YORK, NEW YORK 10007
 ATLANTA CHICAGO DENVER HONOLULU HOUSTON LOS ANGELES NEW YORK
 PORTLAND SALT LAKE SAN FRANCISCO SEATTLE WASHINGTON, D.C.
 ST. JOHN, NEW BRUNSWICK HALIFAX, NOVA SCOTIA DON MILLS (TORONTO), ONTARIO
 LONDON, ENGLAND TEHRAN, IRAN MADRID, SPAIN

 **Kem-Tech Laboratories, Inc.**

AIR AND WATER POLLUTION CONSULTANTS

Environmental Studies • Industrial Plant

Investigations • Mobile Laboratory Surveys


Pre-plant Studies

949 W. McKinley Street Baton Rouge, La. 70802

JACOB KATZ
 AIR POLLUTION CONTROL
 CONSULTING SERVICE
 4525 MAIN STREET
 MUNHALL, PA. 15120 412-462-5816

NEWING LABORATORIES, INC.
 260 ISLIP AVE ISLIP, N. Y. 11751
 SERVICE IN THE SANITARY SCIENCES
 Industrial—Municipal—Private
 Water—Sewage—Food—Air
 Analyses—Research
 Approved by N. Y. State Dept. of Health
 BERNARD NEWMAN, ChE., Ph.D., Director

NUS CORPORATION
Consulting Engineering
 Air Pollution
 Water Pollution
 Environmental Analyses
 Process Design and Evaluation
 Environmental Safeguards Division
 1730 M Street, N.W.
 Washington, D. C. 20036
 Area Code 202 296-8850

REYNOLDS, SMITH AND HILLS
 ENGINEERING DIVISION

*Planning • Reports
 Design • Supervision*
 JACKSONVILLE • ORLANDO • TAMPA
 CAPE KENNEDY • LAKE LAND

 **SINGCO INC.**
 AIR QUALITY INVESTIGATIONS
 Call or write: R. C. Wanta, SINGCO INC.,
 Burlington, Mass. 01803 - (617) 272-5151

(Ads continued on page 864)

**USE THE
 CONSULTANTS'
 DIRECTORY**

1967

Size	RATES PER MONTH	
	6 months	12 months
1" x 1 col.	\$11.75	\$10.75
1" x 2 col.	23.00	21.00
1" x 3 col.	33.00	30.00
2" x 1 col.	23.00	21.00
2" x 2 col.	43.00	39.00

Your card may appear in every issue for one year, every issue for six months (consecutive issues), or every other issue for one year. Send your copy to Alfred E. Gall, ENVIRONMENTAL SCIENCE & TECHNOLOGY, 430 Park Ave., New York, N.Y. 10022, or call him at 212-688-8600.

 **Oceanonics, Inc.** A Division of Engineering Enterprises Incorporated
Consulting & Research in Estuarine and Marine Waste Disposal Problems
 P.O. Box 1095 Morgan City, La. 70380 P.O. Box 4012
 Phone: 384-3362 (504) College Station, Texas 77840

PROFESSIONAL CONSULTING SERVICES

(Continued from page 863)

John F. Dequaine, Fishery Biologist

Specialist in pollution
affecting aquatic life
Biological—Fisheries Surveys

SOUTHERN FISH CULTURISTS, INC.

P. O. Box 251 Phone: 904-787-1360
Lecsburg, Florida 32748

H. GLADYS SWOPE CONSULTING CHEMIST

Waste Management and Pollution Control
214 N. ALLEN STREET MADISON, WIS. 53705
PHONE: AREA 608 238-9986 or 222-6018

Water, Sewage, Stream Pollution
Industrial and Radioactive Wastes
Industrial Waste Surveys

THORSTENSEN LABORATORY

Waste Disposal Problems In:

Chemical, Leather, Paper
and Textile Industries

Member: American Council
Independent Laboratories

P.O. Box 267 Lowell, Mass. 01853



**TRC
SERVICE
CORPORATION**

PERSONNEL, COMPUTING, AND LABORATORY FACILITIES FOR AIR POLLUTION SERVICES

- Tests • Evaluation
- Surveys • Recommendations

Affiliate of The Travelers Research Center, Inc.
250 Constitution Plaza, Hartford, Conn. 06103
Telephone (203) 277-3771

YORK RESEARCH CORPORATION

Air and Water Pollution Services

Laboratory Analysis Monitoring
Industrial Plant Investigations

One Research Drive, Stamford, Conn. 06904
Conn.:(203) 325-1371 N.Y.C.:(212) 635-6378

USE THE CONSULTANTS' DIRECTORY

1967
RATES PER MONTH

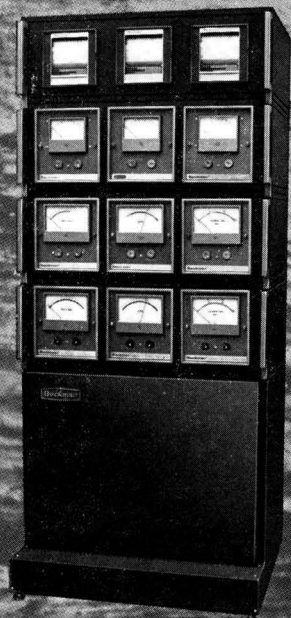
Size	6 months		12 months	
	months	months	months	months
1" x 1 col.	\$11.75	\$10.75		
1" x 2 col.	23.00	21.00		
1" x 3 col.	33.00	30.00		
2" x 1 col.	23.00	21.00		
2" x 2 col.	43.00	39.00		

Your card may appear in every issue for one year, every issue for six months (consecutive issues), or every other issue for one year. Send your copy to Alfred E. Gall ENVIRONMENTAL SCIENCE & TECHNOLOGY, 430 Park Ave., New York, N.Y. 10022, or call him at 212-688-8600.

INDEX TO ADVERTISERS IN THIS ISSUE

Atlas Electric Devices Co.	855	Professional Consulting Services	863, 864
Kreicker & Meloan, Inc.		John J. Baffa, Consulting Engineers	
		Betz Laboratories, Inc.	
		Dames & Moore	
		Engineering-Science, Inc.	
		Carl R. Flodin	
		Jacob Katz	
		Kem-Tech Laboratories, Inc.	
		Newing Laboratories, Inc.	
		NUS Corp.	
		Oceanonics, Inc.	
		Reynolds, Smith and Hills	
		Cyrus Wm. Rice & Co.	
		Singco Inc.	
		Southern Fish Culturists, Inc.	
		H. Gladys Swope	
		Thorstensen Laboratory	
		The Travelers Research Center, Inc.	
		York Research Corp.	
		▼ ▼ ▼	
		Advertising Management for the	
		American Chemical Society Publications	
		REINHOLD PUBLISHING CORP.	
		A Subsidiary of Chapman-Reinhold, Inc.	
		430 Park Ave., New York, N.Y. 10022	
		Phone: (Area Code 212) 688-8600	
		Cable Address: REINPUB NYK	
		Thomas N. J. Koerwer	
		Advertising Sales Manager	
		J. Barry Stanford	
		Assistant Advertising Sales Manager	
		SALES REPRESENTATIVES	
		Chicago 60603 . . . Laurence O. Roberts,	
		Joseph C. Hoopes, Reinhold Publishing	
		Corp., 10 S. LaSalle St. (Area Code 312)	
		726-1282.	
		Denver 80203 . . . Robert H. Heidersbach,	
		Roy McDonald Associates, Inc., 846	
		Lincoln St., (Area Code 303) 826-3325	
		Houston 77006 . . . Frank N. Vickrey,	
		Richard Clothier, Roy McDonald Associ-	
		ates, Inc., 3130 Southwest Freeway,	
		(Area Code 713) 529-8711.	
		Los Angeles 90045 . . . Clay S. Holden,	
		Reinhold Publishing Corp., 8939 S.	
		Sepulveda Blvd., Suite 528. (Area Code	
		213) 776-0552.	
		New York 10022 . . . Thomas N. J. Koer-	
		wer, J. Barry Stanford, Edward L. Can-	
		ova, Reinhold Publishing Corp., 430	
		Park Ave. (Area Code 212) 688-8600.	
		San Francisco 94109 . . . Gerald E. Parsons,	
		Reinhold Publishing Corp., 1255 Post	
		St., Suite 625. (Area Code 415) 771-	
		7044.	
		Tulsa 74114 . . . Max C. Nelson, Roy Mc-	
		Donald Associates, Inc. 2570 S. Harvard	
		Ave. (Area Code 918) 724-9961.	
		PROMOTION DEPARTMENT	
		Robert L. Voepel	
		Promotion Manager	
		PRODUCTION DEPARTMENT	
		Alfred E. Gall	
		Advertising Production Director,	
		ACS Publications	
Beckman Instruments, Inc.	850: 856: 3rd Cover		
Hixson & Jorgensen, Inc.			
The Bendix Corp., Scientific Instruments			
Div.	851		
MacManus, John & Adams, Inc.			
Bowser-Briggs Filtration Div.	853		
E. H. Brown Advertising Agency, Inc.			
Burdick & Jackson Laboratories, Inc.	857		
Studio 5 Advertising			
Calgon Corp.	776		
Ketchum, MacLeod & Grove, Inc.			
Clinet Instruments, Inc.	862		
Saratoga Advertising			
Dow Chemical Co.	770		
MacManus, John & Adams, Inc.			
Drummond Scientific Co.	858		
Ed. Kehl Advertising Agency			
Hewlett-Packard, Analytical Instruments			
Richardson, Thomas & Bushman, Inc.	772		
Nalco Chemical Co.	2nd Cover		
Foley Advertising, Inc.			
Science Pump Corp.	852		
John B. Ferguson, Inc.			
The Staplex Co., Air Sampler Div.	857		
R. E. McGuire Associates, Inc.			
Technicon Corp.	767		
Mediad, Inc.			
UOP.	4th Cover		
Gallay Advertising, Inc.			

The new highwater mark in water quality monitoring:



pH
ORP
Chloride
ion
DO

Temperature
Turbidity
Solar Radiation
Conductivity

continuous automatic analysis
of up to 9 parameters simultaneously

recorded by the new Beckman Model 9500

Water Quality Monitor

Modular design allows the monitor to be adapted to the specific requirements of any single application. It can monitor as few or as many parameters as desired.

Convenient, see-through flow chambers are easily assembled/disassembled for cleaning or buffering of electrodes or replacement of sensors. Sample flow and condition of sensors can be checked without interrupting measurement.

All amplifiers have large indicating

meters which allow easy on-site calibration and trouble-shooting. 4-20 ma DC output from all analyzers assures signal compatibility with multi-point large case or miniature current recorders and telemetering systems. All parameters may be recorded by multiple pen recorders, providing continuous easy-to-follow trend read-out for each parameter.

These and other design features are the result of extensive Beckman experience in analytical instrumentation and process control. And this knowhow is backed by the worldwide Beckman sales and service organization to support your continuing needs. For complete information, contact your local Beckman Process Sales Engineer or write for Data File PW-16-168.

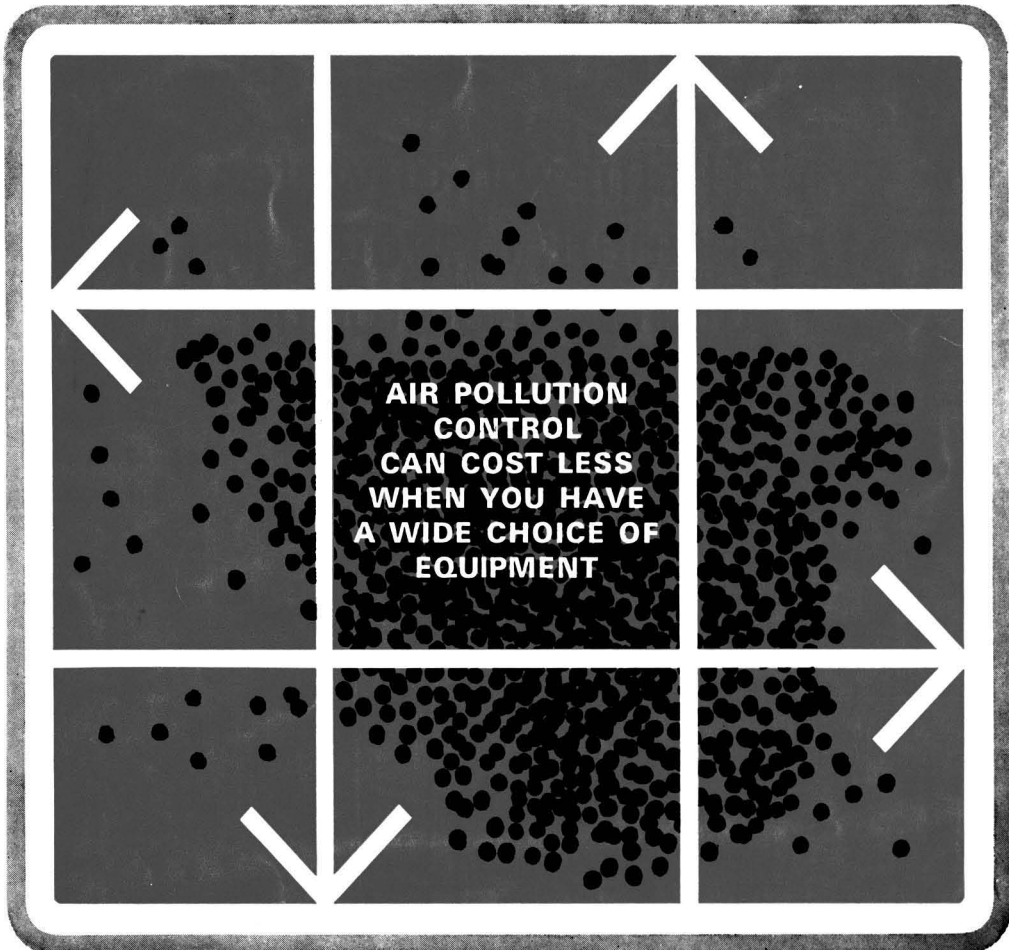
Beckman

INSTRUMENTS, INC.

PROCESS INSTRUMENTS DIVISION

FULLERTON, CALIFORNIA • 92634

INTERNATIONAL SUBSIDIARIES: GENEVA; MUNICH; GLENROTHES,
SCOTLAND; TOKYO; PARIS; CAPETOWN; LONDON; MEXICO CITY



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

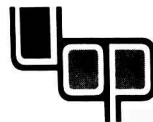
If the pollutant is a gas, for example, you may have a choice between wet scrubbing, catalytic or thermal incineration and carbon absorption. If it's a dust problem, for example, you may have a choice between centrifugal collection, precipitation, filtration and wet scrubbing.

But which one will cost you less?

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

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

the better ideas are at



Circle No. 8 on Readers' Service Card