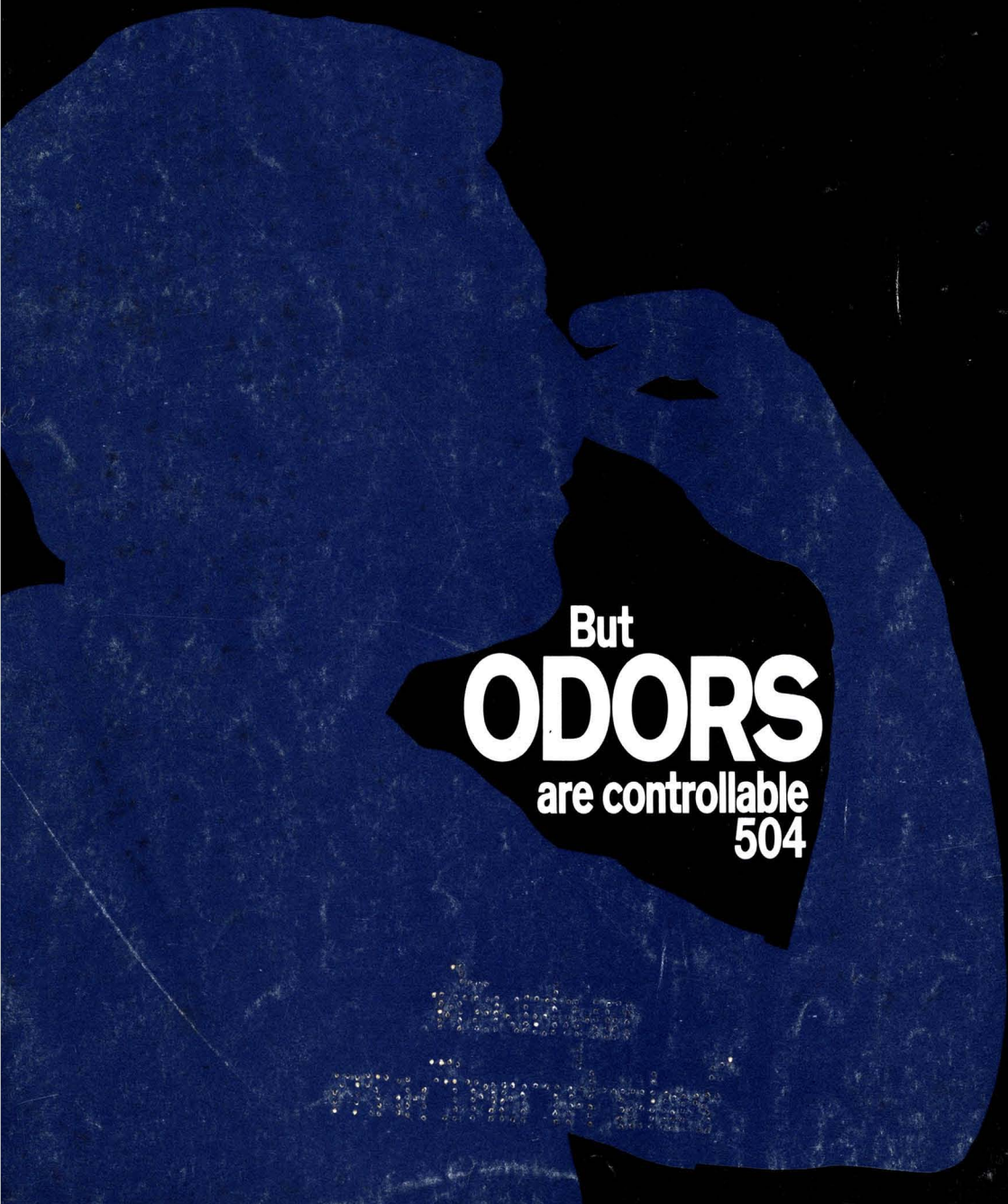


Environmental

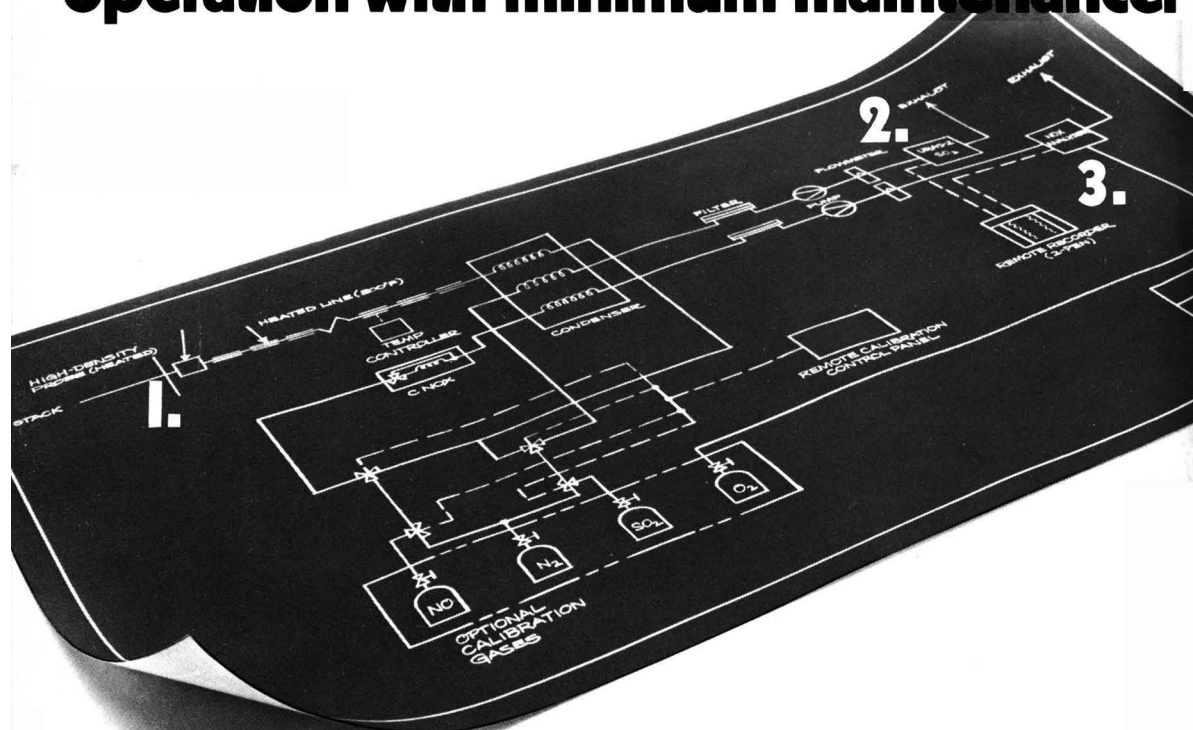
Science & Technology

JUNE 1973



But
ODORS
are controllable
504

Let Intertech build you a stack monitoring system like this. It will give you reliable, accurate and automatic unattended operation with minimum maintenance.



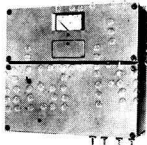
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June 24-28, 1973

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BOOTH 1213 See Advertisement on Page 564

CIRCLE 27

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BOOTH 908-909 See Advertisement on Page 559

CIRCLE 13

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CIRCLE 22

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BOOTH 310 See Advertisement on Page 501

CIRCLE 26

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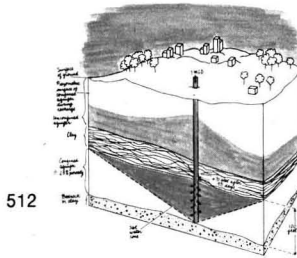
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CIRCLE 39

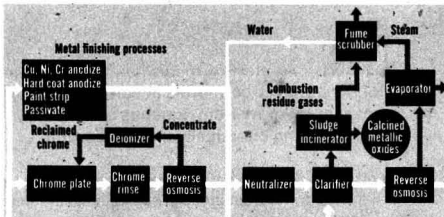
Environmental Science & Technology

Volume 7, Number 6, June 1973

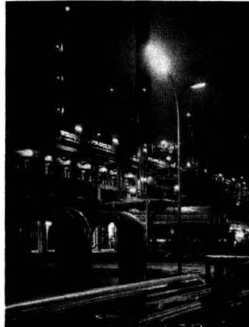
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RESEARCH BRIEFS

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Ammonia in surface waters, sewage samples, and saline waters is measured with an ammonia selective electrode. This method is preferable to the indophenol blue method.

The collection and determination of sulfur dioxide by combining permeation with the West-Gaeke procedure are worked out by Kenneth D. Reiszner and Philip W. West, Louisiana State University 526

A method to measure average pollutant concentrations directly for a desired study period is developed for sampling and determining sulfur dioxide in the ambient atmosphere. The procedure is simpler than previous methods and requires less equipment.

Kyong C. Chun and James E. Quon at Northwestern University study the capacity of ferric oxide particles to oxidize sulfur dioxide in the air 532

The heterogeneous oxidation of sulfur dioxide in air by ferric oxide particles, generated by the combustion of iron pentacarbonyl, is investigated. The reactor's capacity is 62.2 m/mg FeO_3 .

Stimulated biodegradation of oil slicks using oleophilic fertilizers is studied by Ronald M. Atlas and Richard Bartha at Rutgers University 538

A combination of paraffinized urea and octylphosphate is used to promote oil biodegradation in laboratory experiments and in field trials. The practical application of this principle to oil cleanups appears to be feasible.

Yoshinari Ambe at Tokyo Metropolitan University examines a method to determine alkylbenzenesulfonate (ABS) in bottom sediment 542

A new method for the analysis of alkylbenzenesulfonate (ABS) in river, lake, and sea bottoms is examined and its applicability verified. Concentrations of methylene blue active substance are determined and MBAS/ABS ratios compared to find the net content of ABS.

The permeation of sulfur dioxide through polymeric stack sampling interfaces is carried out by Charles E. Rodes, Richard M. Felder, and James K. Ferrell at North Carolina State University 545

The use of a cylindrical polymeric tube as a permeable interface between a stack and a continuous ambient sulfur dioxide monitor is investigated. Results indicate the tube is a promising device for stack monitoring.

Chemiluminescent reactions of peroxyacetyl nitrate and ozone with triethylamine as a possible atmospheric monitor for peroxyacetyl nitrate are studied by James N. Pitts, Jr., Hartmut Fuhr, Jeffrey S. Gaffney, and John W. Peters at the University of California, Riverside 550

Chemiluminescence spectra from the gas phase reactions of peroxyacetyl nitrate (PAN) and ozone with triethylamine are obtained at atmospheric pressure. Concentrations of PAN as low as 6 ppb are detected by this method.

NOTES

Earl J. Roberts and Stanley P. Rowland at the Southern Regional Research Laboratories in New Orleans discuss the removal of mercury from aqueous solutions by nitrogen-containing chemically modified cotton 552

The effectiveness is studied of cotton cellulose modified with 2-diethylaminoethyl or 2-aminoethyl substituents in removing mercury from aqueous solutions in concentrations above 1000 ppb. It was more effective than three other celluloses.

CORRESPONDENCE

An earlier paper on the identifying sources of lead contamination by stable isotope techniques is criticized by E. B. Rifkin and Gary Ter Haar of the Ethyl Corp., and responded to by the original authors, M. B. Rabinowitz and G. W. Wetherill of the University of California, Los Angeles 555

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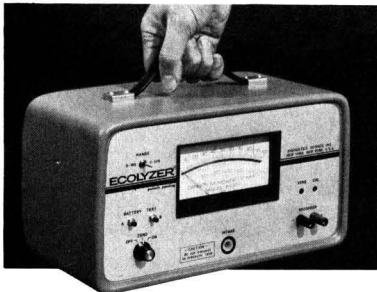
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On one hand we are told that the air is getting cleaner and we wonder if it is really so. On the other, we hear of relaxation of standards and time extensions for deadlines, and we wonder how the two can be compatible.

On the basis of monitoring data, EPA says that the air is cleaner today than it was in the past. There is a 50% improvement in the SO_x level as well as a 20% improvement in the particulate matter level in urban areas, but no measurable progress in nonurban areas. The SO_x improvement is based on monitoring data from 32 urban areas of a 1964 level in comparison with a 1971 level. The particulate matter improvement is based on 12-year data—a comparison of a 1960 level and a 1971 level for 116 urban areas.

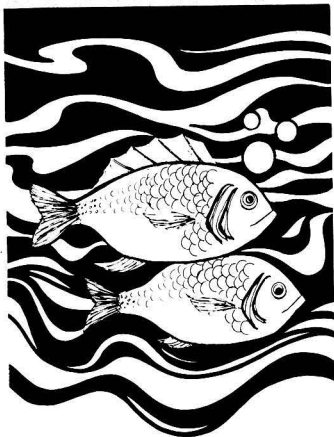
But the clean fuels policy needed to meet the U.S. mandated cleanup goal by mid-decade doesn't seem to be in the cards. There may not be enough fuel to go around, let alone clean fuel. Governors in various states with dirty air areas may have to extend their deadlines, at least those specified in the secondary standards which, after all, are required only at a reasonable time after achievement of the primary standard by mid-1975.

Research results have now upset standards already set. Revisions in the NO_x analytical procedure, the proposed relaxation of the secondary standard for SO_x, and the one-year extension granted to auto manufacturers come to mind.

The air degradation issue remains unsettled. One view maintains that the "protect and enhance" language in the preamble of the legislation should be read and applied together in a real-time situation. Then, in dirty air areas both the protection and enhancement would apply; in pristine areas the air could be protected but not enhanced. Hence, it has been suggested that the antidegradation issue is not needed and no more time should be spent on it. Simplistic language, simplistic tests, and simplistic examples seem long overdue.

Later this month, at the annual meeting of the Air Pollution Control Association, more technical progress will become apparent.





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Incineration or pyrolysis

Dear Sir: In the feature article entitled "Solid waste disposal: incineration or pyrolysis" (ES&T, April 1973, pp 308-12), the author makes a statement which is not borne out by fact. On page 310, he refers to Federal regulations requiring new incinerators to emit flue gas with a particulate matter concentration not greater than 0.08 gr/scf, corrected to 12% CO₂.

Mr. Fife does not point out that this regulation covers only dry filterable particulate matter, and does not include the solubles which are gathered by the impingers in the sampling train. Under previous regulations, this emission figure was higher, since it used to include all particulate, dry and soluble. Continuing on, he states flatly that "Starved-air systems meet this requirement without gas cleaning equipment, while conventional furnaces require wet scrubbers or electrostatic precipitators with 99% efficiency for compliance." This statement is misleading as well as false.

Obviously, Mr. Fife did not do all his homework before making that statement. I cannot speak for other incinerator manufacturers, but I can say that we at Federal Enterprises do make a conventional, retort-type incinerator, which can and does meet the regulations referred to in the article.

Our units have been tested in various sizes in locations throughout the country, and they have consistently met the codes. In addition, they have met the 0.08 gr/scf restriction not only when measured as dry particulate, but when total particulates were considered, as well.

I was distressed to think that an uninformed individual reading Mr. Fife's article might pass a blanket judgment against so-called "conventional" incinerators, based on these statements. I was also distressed to see that Federal Enterprises' name was not shown on the list of incinerator manufacturers, since we manufacture what is considered by some to be the highest quality conventional-type incinerator built today.

C. R. Ragland
Vice-president
Federal Enterprises, Inc.
Nixa, Mo. 65714

Dear Sir: We noted, with a great deal of interest, Mr. Fife's paper entitled "Solid waste disposal: incineration or pyrolysis" (ES&T, April 1973, pp 308-12). The technical content of his paper was excellent, but omits any mention of the DEVCO system of pyrolysis.

The complete DEVCO system, developed over a period of five years, includes front-end separation of corrugated fiber and mixed paper fiber —pyrolysis of the reject material— then separation of the char into the inert, ferrous, nonferrous, and carbon elements. The system is capable of producing a little over 1 lb of steam (400 psi saturated) for every pound of refuse, and recovery of storable carbon fuel.

DEVCO has the largest operating pyrolysis system in the world, capable of receiving and processing refuse at the rate of 7½ tons/hr. This system has been in operation for almost two years in Flushing, N.Y. (the front-end separation subsystems were tested in pilot plants located in Upland, Calif., and Brooklyn, N.Y.).

The Federal EPA, New York State Environmental Conservation, New York City EPA personnel plus representatives from numerous other states and cities have visited the Flushing plant and witnessed it in operation.

DEVCO is currently in negotiations for full-scale systems in several locations. We anticipate a sales volume of \$18 million this year.

DEVCO plans to own and operate most of its plants, under contracts with municipalities for dumping fees, in most cases, below present costs. Revenue sharing, in the form of recycled material sales rebates, is offered on a negotiated basis.

Numerous studies have shown that pyrolysis is the most controllable means of refuse reduction, offering resalable by-products and low capital costs as advantages, while keeping in pace with current ecological conservation goals.

Key patent claims are pending on the DEVCO system.

W. Wayne Morgan
Vice-president
Devco Management Inc.
New York, N.Y. 10022

CURRENTS

WASHINGTON

President Nixon's energy message proposed taking at least three major steps that could have serious environmental consequences. He ordered the Interior Department to seek to triple offshore acreage under federal oil and gas leases, recommended the licensing of offshore deep water ports, and appealed for swift action on an Alaskan oil pipeline. All three proposals have come under fire from environmentalists. As to other actions, the report scrapped restraints on oil imports, proposed that Congress remove federal price ceilings from new natural gas supplies and extend the investment tax credit to cover drilling for new oil and gas fields. Mr. Nixon, in the report, also promised to renew his 1971 request for an overall Department of Natural Resources.

The EPA has taken action to clean up one of the country's largest single sources of air pollution—the U.S. Steel complex in Gary, Ind. The U.S. Steel Gary Works and the Universal Atlas Cement Division of U.S. Steel Buffington Harbor Station were issued a 30-day notice that they were violating federally enforceable state air regulations. The notice claimed that more than 70,000 tons of particulate matter per year were being emitted at 21 different sites within the U.S. Steel complex. The EPA also has proposed that states set up procedures, prior to construction of stationary source facilities that may generate significant amounts of auto traffic. The proposal would assure that standards set up by the Clean Air Act amendments of 1970 would be maintained in the vicinity of a major new facility.

New forms for waste water disposal permits have been issued by the Environmental Protection Agency. A Standard Form "A" is to be used by cities with populations of more than 10,000. A Standard Form "C" is to be used by businesses and industries that already have filed Short Form "C" or "D" if their discharges total more than 50,000 gal a day, contain toxic substances, or affect the waters of another state. As of April 23, permits also are required for dumping waste materials into the oceans. Exceptions to this requirement are municipal or industrial sewage out-

falls that are required to have waste water discharge permits under the Water Pollution Control amendments of 1972.

EPA's new acting head, Robert W. Fri, says he will not keep the directorship longer than two months. Fri, formerly number two man at EPA, accepted the post temporarily after



EPA's Fri

William D. Ruckelshaus was picked by President Nixon to head up the FBI. Fri says he plans to leave EPA soon to return to his previous job as a partner at McKinsey and Co., Inc.

More mine-scarred land will be reclaimed for recreational purposes. The Interior Department has awarded four additional grants under its program. A \$329,355 matching grant for Whitley County, Ky., will be used to help create a 334-acre multifacility park from lands now badly scarred by strip mining. In King County, Wash., a \$300,000 grant will cover half the cost of reclaiming 19 acres of surface-mined land near Redondo Beach that will be used as a recreational area. A \$126,710 grant was awarded to Spokane County, Wash., to help officials there convert 24 acres of abandoned gravel pit land into a recreational park. And Kellogg, Idaho, was awarded \$69,167 to help prepare a 26-acre mine tailings deposit area on the South Fork of the Coeur d'Alene River for public and school recreational use.

The Tennessee Valley Authority has started construction work on a \$32-million program to improve air pollution control at its Johnsonville, Tenn., steam plant. The project calls for electrostatic precipitators to be added to all 10 generating units at the plant to meet new Tennessee standards for controlling emissions of fly ash particles. The first stage of the work will be to install precipitators on the plant's four largest generating units.

STATES

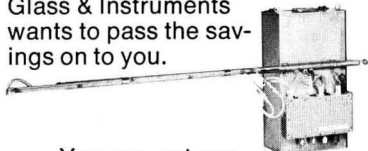
The Illinois Senate rejected the appointment of Mary Lee Leahy as director of the state EPA. Illinois Governor Dan Walker charged that "the politics of protecting the special interests and the politicians" are responsible for the Senate rejection. According to the Governor, Mrs. Leahy, during her 100 days in office, questioned pollution control programs in Chicago: The city was not complying with a city-state agreement to provide the state with data from surveillance and investigations; much of the city's equipment, purchased with \$1 million of federal funds, was lying around unused; the city was keeping secret results of investigations on individual polluters; the city did not supply the state with records of citizen complaints; and the 1973 grant application to the Federal Government did not include goals to abate pollution. The governor is reporting the situation to the Federal Government.

Michigan's Wayne County Department of Health is suing International Salt Co. (Detroit) for excessive emissions of salt. The company, operating the world's largest salt mine, is charged with 18 violations of the county's regulation for emissions of salt dust and other related aerosols from open storage piles and salt processing and transporting activities. Language in the suit calls for shutdown of the mining and processing operations if the company fails to comply with temporary and permanent controls. **A bill in the Nebraska legislature would give tax incentives to** gasohol—a blend of 10% ethyl alcohol made from grain and 90% gasoline. Also, Farmland Industries (Kansas City, Mo.), a farm cooperative representing about 500,000 Midwest farmers, is "actively considering the use of gasohol."

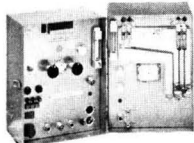
The right of the Pennsylvania Department of Environmental Resources (DER) to order coal mines to treat acid mine drainage which does not originate in their mines but which must be pumped out to enable the mines to operate was upheld in that state's supreme court. The precedent-setting decision, which reversed the opinion of a lower court that the state was depriving companies of the use of their property, will have an effect on

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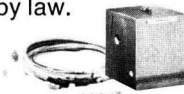
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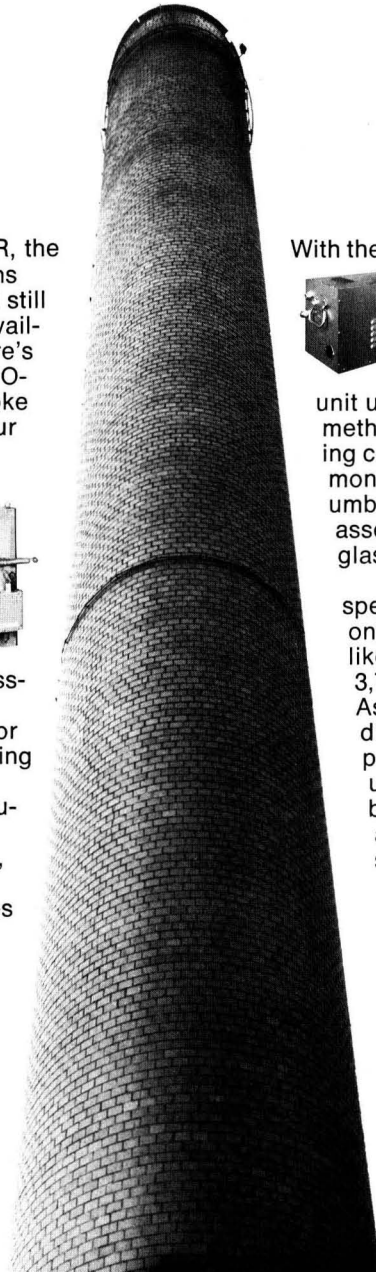
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environmental issues other than acid mine drainage, according to DER. **Delaware's first pollution control bonds will finance** waste treatment projects for the Industrial Chemicals and Specialty Chemicals plants of Allied Chemical Corp. The \$9.2-million issue is the company's first venture into industrial-revenue-bond financing for pollution control.

A Florida county will have the "nation's most sophisticated solid waste shredding and resource recovery system on a municipal scale." The \$6.8-million shredding, resource recovery, and landfill complex will handle solid waste disposal through the year 2000 in rapidly growing Brevard County which includes the Kennedy Space Center and Disney World. **A \$564,000-transfer station opened in Allegheny County, Pa.,** last month. It's the first of four such stations. Partially operated by a federal EPA demonstration grant, the transfer station system could save \$750,000 annually in waste handling costs. According to Pennsylvania officials, EPA's grant is the first such allocation for solid waste implementation in the U.S.

Twelve Ohio operators of coke oven facilities have been given 30 days by the state EPA to submit acceptable plans and schedules for cleanup of air pollution. The required timetables must outline when and how the facilities will meet applicable air pollution standards and regulations as set by the Federal Government and the Ohio EPA.

The Illinois Pollution Control Board assessed Ralston-Purina Co. \$7500 for odor and dust emissions and for operating without a permit from the Board. Evidence indicated that odor and dust nuisances had remained unabated for approximately 20 years. **In Minnesota, a statewide regulation banning the use of asbestos** in certain phases of construction work was approved. The regulation also requires the use of baghouse filters to prevent asbestos emissions from manufacturing plants.

RESEARCH

"Lead may be essential for growth" and "no tie between lead in blood and lead in air" are recent findings from two studies. Klaus Schwarz of the UCLA School of Medicine is responsible for the first quote in a letter to

the EPA on health effects of airborne lead. Over the past few years, Dr. Schwarz has been active in research that has led to the identification of chromium, selenium, tin, vanadium, fluorine, and silicon as elements necessary for growth and general development. The second quote comes from the final report of the worldwide research organization of the lead industry, the International Lead Zinc Research, Inc. Philip Robinson, executive vice-president of the Lead Industries Assoc., said, "The study clearly shows that removal of lead from gasoline would have no impact on the blood lead levels of the population."

CONSULTING

Geraghty & Miller, a firm of consulting groundwater specialists, is performing a 14-month study of groundwater contamination problems in 11 northeastern states which account for 26% of the nation's population. Project leader David Miller says, "No one really knows how severe the groundwater contamination problem is in the Northeast and one of the goals of the study is to put this problem in its proper perspective."

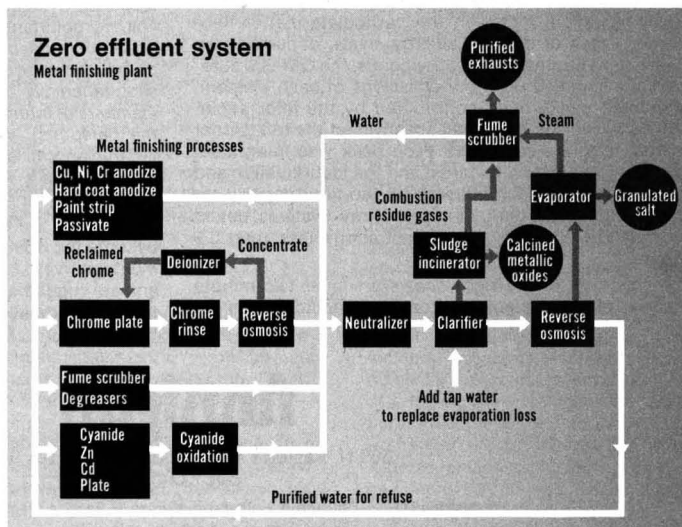
Shredding and landfilling wins out over incineration, according to the consulting engineering firm of Leonard S. Wegman Co., Inc. In their analysis for the city of Miami, Fla., air pollution

could be "reduced by a factor of five—from 3911 lb net emission for incineration to 757 lb net emission for shredding, assuming credits for use of waste heat steam," Wegman says. Of course, the shredding and landfilling are suitable only where nearby adequate land is economically available. In the case of Miami, shredding and landfill amounted to \$7.27/ton vs. \$9.07/ton for incineration.

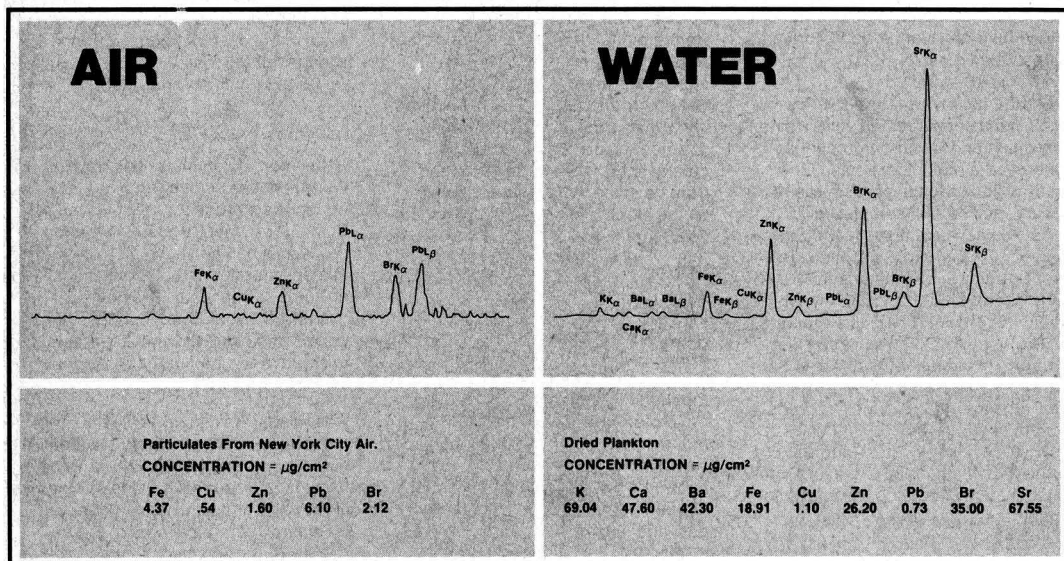
TECHNOLOGY

Sulfur-containing impurities from industrial gases can be removed, according to a process patent issued to Bethlehem Steel Corp. The two-step process is being used in a coke-oven gas desulfurizer at their steel plant at Burns Harbor, Ind. The new process uses a sodium carbonate solution as an absorbent and steam jets to achieve a vacuum; the old process involved three steps.

A zero effluent discharge system in the metal finishing industry has been put into operation at the U.S. Army's Rock Island Arsenal in Illinois. Water is recycled and all wastes are reclaimed. Operational cost of the Arsenal's metal finishing plant have been reduced \$52,000 annually. The fully automated system was engineered by DMP Corp. (Charlotte, N.C.); it will save the Arsenal 54 million gal of water a year, 9% of its total requirement. The system uses the largest reverse osmosis unit ever built for an



Detect and Measure Ten Elements in a Pollution Sample in Two Minutes (Including Sample Preparation)



A Finnigan QM-900 Automated Energy Dispersive X-ray Fluorescence Analysis System detected and quantified trace concentrations of iron, copper, zinc, lead, and bromine in an air pollution particulate sample in less than two minutes. The sample, on filter paper, was simply inserted into the instrument's sample chamber. Under X-ray excitation, atoms in the particulate matter fluoresced X-rays of different energy levels, depending on the element fluorescing. In 30 seconds, the QM-900 automatically summed up X-ray emissions of each element, subtracted background contributed by the filter paper, and displayed the elemental spectrum at the left. Under internal program command, each peak was integrated, compared to stored standards, and the identification and concentration of each element on the filter paper were printed out in $\mu\text{g}/\text{cm}^2$. Finnigan X-ray systems detect and analyze elements at concentrations less than 0.5 $\mu\text{g}/\text{cm}^2$.

The spectrum at the right shows a similar two-minute analysis of dried plankton from the Pacific Ocean off

Monterey, California. In similar fashion, we have analyzed such other water pollution samples as sludge from the Houston Ship Channel and New York's East River, and effluent from a Georgia paper mill.

The Finnigan Automated Energy Dispersive X-ray Fluorescence System is the most efficient solution for high-volume pollutant analysis requirements. *Unlike atomic absorption spectrometry, X-ray analysis is fast, non-destructive, requires little sample preparation and simultaneously measures trace concentrations of all elements of interest (including sulphur, phosphorous and the halogens).* With our automatic sample changer, a technician can analyze 250 samples for 10 elements in an 8-hour day. And, all data is stored and available in digital form for further computer processing if desired.

At Finnigan, we believe that energy dispersive X-ray will become the dominant day-to-day technique for environmental survey. Finnigan X-ray systems begin at \$35,000 and are rugged enough for use in vans and trailers. Contact us for detailed pollutant analysis applications data.

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industrial purpose; the units were manufactured by Osmonics, Inc. (Minneapolis, Minn.).

A SO₂ removal process, the citrate process of the Bureau of Mines, is being installed in pilot plant stage at a lead smelter in Kellogg, Idaho. The process uses a water solution of citric acid and sodium citrate to absorb sulfur dioxide from the gas. Then hydrogen sulfide is added to the solution to procure elemental sulfur, a solid that is easy to ship or store.

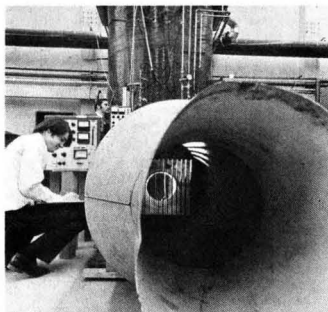
An ozone generator and ultrasonic electrocoagulator is now available for water pollution control applications. Ozonair/Canatraco Ltd. (Montreal, Que.) has a solid state high-frequency system which pretreats the waste water prior to ozonation. Referred to as Film Layer Purifying Chamber (FLPC), the system doubles the concentration of ozone by weight over earlier systems, has a modular design with a maximum capacity of 250,000 gpd, and is finding use in the treatment of waste waters from municipalities and food processors.

Harmful nitric oxide emissions from automobiles can be converted to harmless nitrogen gas with ruthenium catalysts, according to General Motors' researchers. These catalysts are of interest since they avoid the formation of the undesirable compound ammonia; unfortunately, ruthenium is a very rare material which has perhaps insurmountable durability problems for the automotive application.

The passenger car gas turbine engine shows promise of meeting some of the restrictive 1976 federal emission standards, according to four GM engineers in a presentation at the American Society of Mechanical Engineers' Gas Turbine Conference. They caution that even with a major development commitment, it would be an ambitious task to develop a new turbine engine by the 1980's.

NO_x emissions from aircraft can be cut 30% by fuel modification, according to Esso Research and Engineering Co. This reduction involves the use of soluble organometallic derivatives which serve as heterogeneous reduction or decomposition catalysts. These additives may be useful in reducing emissions during takeoff.

An electrostatic precipitator for extremely small particles is being checked by Battelle-Northwest for the federal EPA. Arlin Postma, manager of the study, says, "In our process the air flows through a corona



Precipitator for small particles

charger which imparts a negative electrical charge to the suspended particles which then collect downstream on dry, open-weave fiber beds. The fiber beds are periodically washed in place and the cycle continues."

Solar energy will be used to heat and cool a house in California, under a contract with the Department of Housing and Urban Development. A three-bedroom, split level house will use water ponds on the roof; the system was developed by Harold Hay of Los Angeles. The house will be completed this August at Atascadero where the temperature ranges annually from 10-110°F. In winter, the water ponds are exposed to sunlight and warmed to 85°; heat stored in the ponds radiates uniformly from the ceiling in all parts of the house. In summer, the ponds are insulated to prevent daytime heating by the sun while they are absorbing infiltrated and internally generated heat.

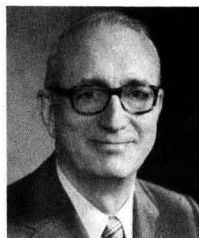
INDUSTRY

The scrap processing industry has labeled the ICC draft environmental impact statement a "sham" as it pertains to iron and steel scrap. The ICC statement finds that all recyclable materials but iron and steel scrap should be granted a 3% holddown on increased freight rates as proposed by the nation's railroads. The Institute of Scrap Iron and Steel maintains that the commission has not followed

its own rules of order since the ICC introduced additional evidence in the impact statement, after the record in the proceeding was supposedly closed.

A leading chemical company is practicing energy conservation. Dow President C. B. Branch told stockholders at last month's annual meeting that the company has "what is probably the most advanced program of energy conservation of any company anywhere." He pointed out that the Midland nuclear plant planned by Consumers Power, a part of the program, will help reduce the heat load to the environment and reduce Dow's own consumption of gas or coal. Branch also said that Dow spent \$17 million on some 400 pollution abatement projects in the U.S. during 1972.

Major setbacks in nuclear power are forecast if nuclear foes prevail. At a recent stockholders meeting in Atlanta, Westinghouse Electric Chairman D. C. Burnham said, "To me it is inconceivable that the opposition of a relatively few people could be



Westinghouse chairman Burnham

permitted to half or even slow down programs in nuclear power which represents man's greatest resource for meeting his future energy needs and one of his most effective tools in the fight against air pollution."

International Paper Co.'s mill at Moss Point, Miss., plans a \$1.2 million improvement program for air and water emissions. According to mill manager H. C. Herring, the program includes a noncondensable gas collection and incineration system which will significantly reduce odors, construction of a cooling tower to reduce the temperature of the water used in the heat exchanges which condense entrained water in the noncondensable gases, and improved pulp washing facilities designed to recycle water by counter-current washing.

How to measure depth, height or thickness with Gaertner optical instruments.

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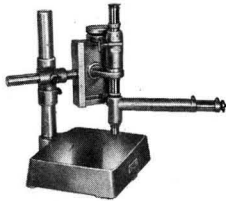
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Measuring Depth?



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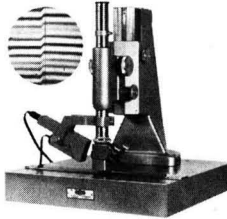
Methods of measurement.

The *draw tube scale* is the simplest. The scale is engraved on the draw tube, with a vernier attached to the microscope body. It reads to 0.005", or 0.1mm. For some applications you might prefer a *dial gage*, actuated by a contact linked with the draw tube, and reading to about 0.0001" For greater range and accuracy, you can have your microscope mounted in a *micrometer slide* with its axis parallel to the slide's precision micrometer screw. Gaertner offers a variety of micrometer slides to solve many measuring problems, plus an extensive selection of accessories for special needs. One example: A *Parfocal Illuminator*, particularly useful where the surface to be focused is difficult to "zero in" on because of roughness.

Applications. Depth measuring microscopes are most effectively used where accuracy in the general range of 0.005" to 0.0001" is required. Typical applications include measurements of hole depth, depth of slots, coating thickness, thickness of transparent materials, thickness of TV tube faces, and etching depth. With a parfocal illuminator, microscopes are ideal for measuring the radii of curvature of lens surfaces and other spherical reflecting objects.

For complete information on Gaertner Measuring Microscopes and accessories, write for Bulletin 161-72. ■

Need finer unit measurements?



Microinterferometer

Gaertner also makes a Microinterferometer for highly precise, non-contacting measuring of surface configuration and thickness of coatings and deposits. This instrument is simple to operate. It uses the principle of interference of light to optically measure in terms of the wavelength of light—measurements to about 1/5th of a wavelength or 2 millionths of an inch. **Ask for Bulletin 209-73. ■**



Ellipsometers

For measurement of ultra-thin films or study of surface phenomena requiring even smaller unit measurements, or for many chemical, biological and biomedical research studies, you'll find a Gaertner Ellipsometer does the job. It uses plane polarized light to achieve readings to a few angstroms. **Ask for Bulletin 203-73. ■**

How to measure vertical distances or displacements... remotely, precisely, without contact.



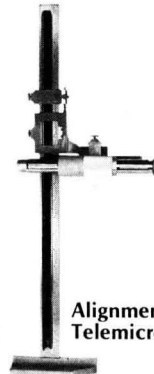
Cathetometers

You can measure the height of objects not accessible to measurement by other means, with a

cathetometer. Measure things you can't touch, like the height of liquids in a tube. Or the deflection of a quartz spring. Or the vertical extension of material under stress—all without physical contact.

A cathetometer consists of a viewing scope (horizontal) mounted on a carriage which moves on an accurate vertical guide. Gaertner cathetometers are offered in a variety of designs with modifications to solve all kinds of difficult vertical measurement problems. The conventional design has a one meter (40") scale with vernier reading to 0.01mm (0.001"). You can focus on objects from 12" to infinity, or shorter distances by substituting a microscope objective.

Versatility. If you wish, we'll provide a small laser in place of the scope, to project a spot precisely at a predetermined level on a large or irregular object such as an automobile body. If you want an optical level reader for more precise leveling, we have it. Or you might want to order your cathetometer with an alignment telescope. And if you want your cathetometer with two scopes, carriages, and verniers, they're available too. **Write for Bulletins 162-73 and 162-66A. ■**



Alignment Telemicroscopes.

Gaertner also offers alignment telemicroscopes which, when used with precision height gages, provide a means of measuring heights without mechanical scriber blade; or for accurately checking alignment of points, apertures, etc., along an axis. **Write for Bulletin 161-73F2. ■**

Information.

We'll be pleased to send specifications and literature on any Gaertner optical measuring instrument of interest to you. Or just ask for our recommendation for an instrument designed specifically to solve your precision measuring problem.

INTERVIEW

Camp Dresser & McKee's Joseph Lawler

What are the basic groups within CDM? Each CDM project is handled by a specially organized team. The firm is project-team oriented, though it does have special support groups—for example, a structural group, an electrical group. A senior officer of the company has responsibility for every design job; he deals directly with the client. A waste water treatment plant, for example, for a city might be a \$20–30 million job. In this case, an officer of CDM at the vice-president level would be in direct charge. Of course, CDM handles all sizes of projects. The firm handles jobs as small as \$5000 in construction costs for many of its clients. Now it wouldn't make sense for the firm to go all the way to Texas for a \$5000 job for a new client, but it makes very much sense for CDM to handle one that size for, say, the town of Andover, 20 miles from Boston, since we have been dealing with them for many years.

How many subsidiaries does the firm have and does the firm have a marketing function? As far as geographic distribution goes, CDM has four offices in the U.S. and seven overseas. CDM also has a partnership. In some states, for example, New York and Virginia, CDM needs a partnership because a corporation cannot operate as effectively there. CDM owns 50% of Camp Scott Furphy, a subsidiary in Australia, and acquired the New York firm of Alexander Potter Associates last year. Potter is a fairly sizable firm of about 60 people and billings of about \$2.5 million. Potter covers the geographical area from New York down to the Washington, D.C. area.

CDM does not have a marketing function, as such. The firm does not have anybody beating the bushes, so to speak, not even one person and never has had. I don't mean to imply that there is anything unprofessional or unethical or anything of the sort; CDM just hasn't found it necessary to do it. Maybe some day we will.

The CDM parent corporation was established in 1970, so we are on our third year as a corporation now. The international subsidiary was set up in 1968 as a corporation, prior to the incorporation of the parent, for various reasons including tax purposes.

Do CDM personnel refer to themselves as environmental engineers, as opposed to sanitary engineers? Yes, in all of our professional cards CDM uses the term environmental engineers. But we still have some clients with whom we use the term sanitary engineer; they prefer the latter terminology.

BUSINESS

What is the current number of active projects and the short-term projection for new construction design under the water law? Current engineering contracts, including reports, total 190; in aggregate they have an estimated construction cost on the

order of \$2.0 billion. Including our subsidiaries, CDM has about \$800 million worth of work under design or construction at this time. Incidentally, the Potter acquisition took place in September 1972, so only the last quarter figures show up in the total figure for 1972 billings.

Is the CDM business 100% in the municipal area, or are there some examples of industrial projects? Private industrial clients have never been a big proportion of the CDM total, although we do have a number of private industrial clients, perhaps representing 5% of our total volume. However, a lot of our municipal plants receive major contributions of industrial wastes and require much engineering study for the industrial wastes alone. Take CDM's job at Niagara Falls, for example. This is a large municipal job; construction costs run over \$50 million. But it is largely an industrial waste problem. About 70% of the waste water which will enter the Niagara Falls plant will



At the helm of one of the largest U.S. consulting engineering firms, Joseph Lawler is president and chairman of the board of Camp Dresser & McKee, a corporation specializing exclusively in sanitary engineering and related sciences, which more appropriately these days has been termed environmental engineering. Lawler tells ES&T's Stan Miller that over the past 20 years, the firm has completed more than 1700 engineering projects and has a current staff of more than 600. With offices in Boston, Washington (D.C.), New York City, Bangkok, Bogota, Dacca, Singapore, Bermuda, and Pasadena, CDM's billings hit \$13 million in fiscal 1972 (calendar year).

be industrial waste. This plant will not use the conventional biological process; it's a physical-chemical treatment plant which will go under construction this year. In fact, it's one of the largest physical-chemical plants—50-mgd—that will be built.

How many advanced waste treatment (AWT) plants does the firm have under design or actual construction? CDM has a lot of them. Major projects where the design has been completed by CDM or its subsidiaries include: a \$41-million plant for Arlington County, Va.; a \$40-million plant for Fairfax County, Va. (both using a combination of biological and physical-chemical processes); two plants for Fitchburg, Mass., totaling \$29 million in cost (one biological-chemical and the other physical-chemical); a \$43-million biological-chemical plant for Chicago, Ill.; and, of course, the physical-chemical treatment plant for Niagara Falls, N.Y. In addition there are a couple of smaller AWT plants on which we are working.

The Salt Creek Plant for Chicago is a CDM design; the plant is under construction now and is of particular interest because it was the first major plant designed utilizing the two-stage aeration process for nitrification with denitrification in a final stage of filtration.

Some of the plants referred to are presently under construction. All of them should be under construction before the end of the calendar year.

What is the current thinking on going public? Any announcement? CDM is definitely "going public." Depending on stock market conditions, the public stock issue will probably take place in the first quarter of 1974, for which we will probably issue about 20% new stock, the remainder of the stock being held within the company.

The firm of White Weld & Co., one of the top underwriters (investment bankers) in the U.S., will handle the operation.

How does CDM go about getting new accounts—by word of mouth, marketing activity, too much business to go around, or what? Most of the business in any good firm comes by word of mouth. When we get a job in a new area that we haven't been in before, and if we do it well, then in due course somebody else comes along and pretty soon CDM may have a number of new clients in an area where we have never worked before.

Obviously, a firm needs to keep its name before the public. One of the best ways to do this is to write technical papers and present them at various professional and technical meetings around the country. Also, if CDM undertakes to submit a proposal for a new project, we make strong efforts to do a really good job on the proposal.

Does the firm have activities or work in most states? At one time or another CDM has worked in the majority of the states, but not all at one time. CDM doesn't make an effort to work in any particular area; it goes primarily by the job. If there is a project that CDM is interested in, and there is a chance that CDM will be considered, then we write letters, send brochures, and if possible meet the key people there so that our firm will be among those considered for the project. Of course, the primary reason for making acquisitions is to get the firm into new geographical areas.

WATER CLEANUP FUNDS

What are your comments on the announced controlled spending of cleanup funds? Will there be enough

funds to go around the sanitary engineering firms? As far as commenting on whether or not the President made the right decision, he is in a better position to judge spending priorities in this country than we are. After all, the funds being made available for water pollution control are still much larger than we have ever had before. There is plenty to do for all of the consulting firms. I'm not personally concerned about this so-called "slow down"; it's all relative to what some people thought was going to happen.

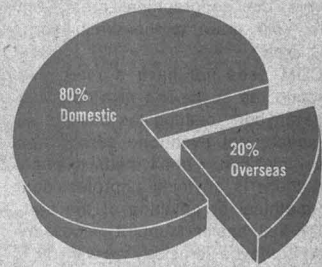
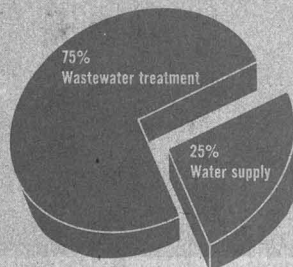
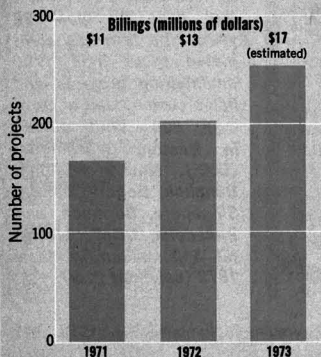
As far as CDM is individually concerned, the firm has a certain rate of growth which we believe we can satisfactorily manage; and if there were 10 times as many jobs available, CDM just wouldn't take them. The firm is not going to grow at a faster rate than it can handle.

TURN-KEY

Does the EPA turn-key proposal have any chance for success? I do not think that turn-key operations for municipal waste water treatment plants are going to work. I want to differentiate between turn-key for municipal waste water treatment and turn-key for waste water treatment for private industry, because there is a vast difference. The turn-key approach for private industry can be quite sound. There are several reasons for this. First, the public interest is not involved. If mistakes are made or if a company makes a bad decision, then no one is hurt but that company. Second, most industrial companies of any size have sophisticated staffs that can properly specify and monitor the turn-key work. And the third and most important reason is that industry doesn't have to take bids for turn-key work, and in most cases they don't. The company can pick from among the top and most reputable

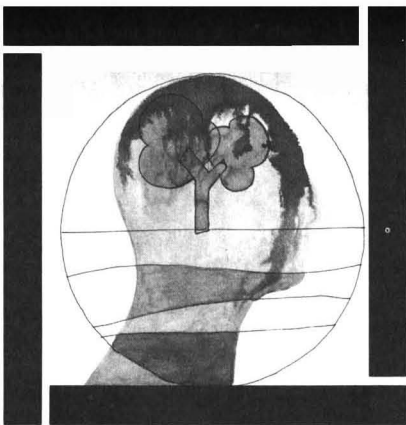
Camp Dresser & McKee, Inc., at a glance

Subsidiaries: Camp Dresser & McKee International Inc. (Boston, Mass.); Camp Dresser & McKee Ltd. (Bermuda, U.K.); CDM Inc. (Pasadena, Calif.); Camp Scott Furphy Pty. Ltd. (Australia); and Alexander Potter Associates Inc. (New York City)



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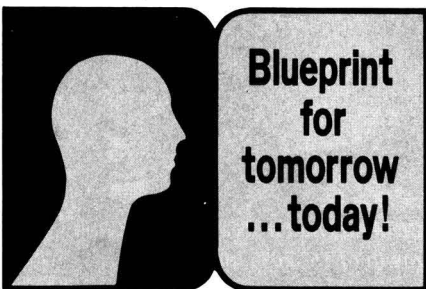
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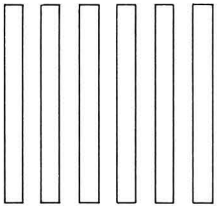
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design construction firms and work something out or negotiate. For all these reasons, industry can usually get a good turn-key job. Industry is not confined in the same way as is a municipal turn-key operation.

But what about turn-key in the municipal area? These same advantages don't work at the municipal end because the municipality will have to go through a bidding situation based on performance standards. In municipal contract work, it is very difficult, and in some cases impossible, to throw out the bids of firms not adequately qualified to do the work; this is where the turn-key approach to municipal waste water treatment plant construction will fail. The municipality may end up with a contractor who may not be really capable of doing the job.

You may want 90% BOD removal, but this performance requirement doesn't enable you to write a specification on every single item that goes into that plant. On a major plant there are literally hundreds of such items as electric motors, pumps, chemical feeders, metering devices, and control instruments. If one could write detailed specifications and make detailed designs on all of these items, then of course you are right back to the conventional approach. The turn-key contractor may get the 90% BOD out but the question is whether the motors, pumps, and ancillary equipment will last for 20 or 25 years. The municipal turn-key operator will install the minimum to last past the guarantee period, three years or whatever is in the contract. With turn-key and public bidding you will not get a long-term low-cost operation. The total life cycle costs will be higher.

Will turn-key actually happen? Turn-key construction of municipal waste water treatment plants is probably going to happen in spite of it all because EPA has obviously made the judgment that it will work. I say that it won't work, but it will probably be several years before the problems show up. First, some municipal plants must be built by the turn-key method and operated for awhile; then the problems will become evident. Ten years from now there won't be any more waste water turn-key work in municipalities—maybe even sooner than that. In the meantime, the mistakes are going to have to be made.

When turn-key becomes part of the EPA operational policy, I predict that there will be a tremendous tendency on the part of many municipalities to go this route because it appears on the surface to be simpler. Many of the smaller municipalities don't have the professional staffs or the degree of technical sophistication to know what they really want, and then to follow up and be sure that they are getting the best. Some do, of course. Many of the larger cities, such as New York and Chicago, are first rate in the waste water treatment field, but there are those that just don't have that kind of expertise.

What can you tell ES&T readers about CDM's new construction management service? Construction management goes far beyond the usual job supervision. Let me give an example. CDM is providing construction management services on both the Fairfax County and Arlington County waste water treatment projects in Virginia. On those projects, which are both large ones, CDM has packaged the work into a number of smaller construction contracts to obtain more competition in bidding. Equipment, piping, pumps, and the like are being purchased ahead of time. Experience on these projects has shown that lower costs are being obtained by using several smaller contractors than by using one large one.

The construction manager is responsible for making sure that all of the equipment gets to the job in the right place at the right time, that the work of the many contractors is coordinated, that the mountain of paper work and project administration is carried out in timely fashion, and that the work is being coordinated with federal, state, and local government officials. One important aspect is that the construction manager be a part of the project from the beginning. A number of other civil engi-

neering consulting firms are now providing construction management services.

OVERSEAS

From your first-hand experience as president of the international subsidiary, how did the company get into this facet of the business? CDM started in the overseas work in 1964. There were a number of reasons for moving in this direction. We felt that there was going to be a big future in the waste water and water supply fields in many of the developing areas of the world. We started responding to overseas invitations. Our first job was in East Pakistan (now Bangladesh), and, by the way, we are still there. CDM has also worked in many other countries including Australia, Brazil, Singapore, Thailand, Canada, Ireland, Taiwan, Turkey, Colombia, Puerto Rico, and the Virgin Islands.

The overseas work averages about 20% of our total volume; half is in the waste water treatment field, and the other half is in water supply. The two biggest jobs that CDM has overseas right now are both water supply—a \$100 million job in Bangkok and a very large water filtration plant (840 mgd) for Sydney, Australia, which will be the third largest in the world. (The two largest are in Chicago.)

ACQUISITIONS

Basically, what type of company does CDM look for in acquisitions? What elements of their operations would be an expansion for CDM? CDM is looking for firms that are exclusively in our field; this is one policy that we adhere to strictly. We don't want to diversify into other fields and therefore we aren't interested in acquiring any firm that's even partly outside the environmental field.

The primary reason CDM is interested in the acquisition of other firms is to move into new geographical areas. There are two basic ways to move into new areas. One way is to develop an office from scratch, as we did in California. This is a long process. The other way is the acquisition route.

Geographically, CDM has divided the country into seven principal areas. We have worked in all those areas in one way or another, but it is difficult to develop much ongoing work without an office in the area. We therefore have long-range plans to establish branch or subsidiary of-

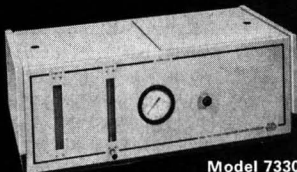
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ENVIRONMENTAL
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fices in each of these areas. Most of the proposed new offices will involve acquisitions, which, in turn, are tied in with our plans to go public.

Our most recent new office is in Washington, D.C. CDM has recently agreed in principle to acquire a firm in Singapore and one in Saigon; CDM would like to participate in the new redevelopment/reconstruction program in South Vietnam.

We also might be interested in acquiring companies which would complement our technical strengths—companies which specialize, for example, in groundwater, irrigation, and R&D. The primary reason for CDM's going public is to obtain the additional capital and public stock to enable us to move in these directions.

NEW TECHNOLOGY

To what extent are new processes being incorporated into the CDM design projects? There has been much talk, particularly from EPA, that consultants are too much inclined to use the old "tried and true" methods, and that by going to the turn-key approach, more "innovative" designs will be forthcoming. The idea that turn-key will suddenly generate exotic new designs that consulting engineering firms cannot themselves produce is, in my opinion, sheer nonsense. Sure, consulting firms failed to turn out very many advanced designs in the past, but that was because there was little or no expressed need for them—water quality standards, by and large, didn't require such advanced designs in the past. But the better consulting firms are certainly turning out such designs today.

In the case of CDM, we like to think that our designs are as "innovative" as any being turned out today. We have a design review committee comprised of some of the top professionals in our firm. This committee keeps on top of all of the latest developments in the field.

As to some examples of new processes being incorporated into CDM projects, I have already mentioned the two-stage aeration process for the Salt Creek plant being constructed in Chicago, in which nitrification takes place in the second aeration stage. In a third stage, filtration, the nitrates will be reduced to nitrogen, passing off as nitrogen gas. This was the first major plant in the country to be designed using this process. One of the plants we have since designed for Fitchburg, Mass., utilizes a similar two-stage aeration process.

To what extent is CDM involved in air pollution control and solid waste disposal projects? On the whole, CDM is not heavily involved in air pollution control. But the firm does a fair amount of work in the solid waste field. For example, CDM recently completed a major study for Erie-Niagara Counties, which includes the city of Buffalo and hundreds of industries in the area. The study featured a computer program for collecting and transporting the wastes and for locating transfer stations.

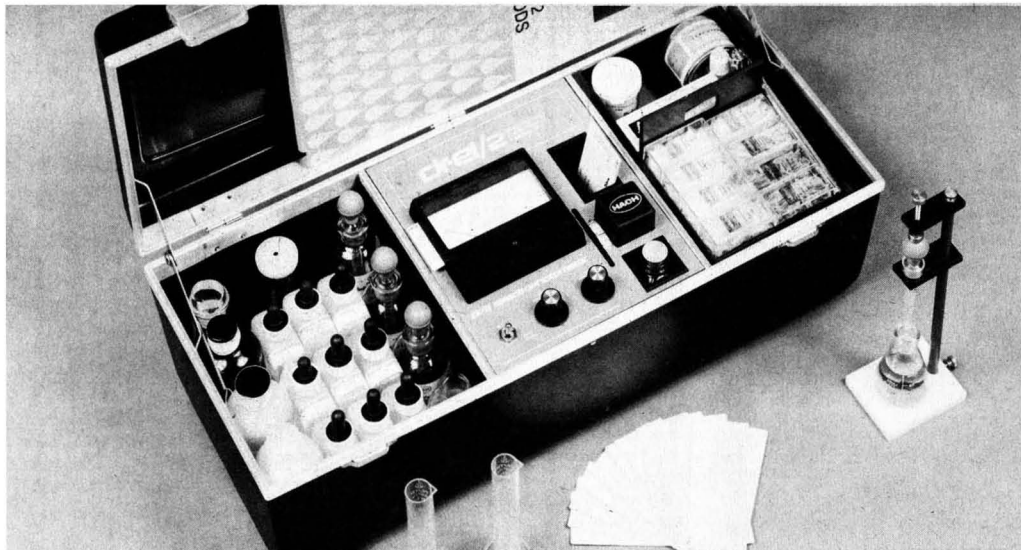
CDM is currently serving as a consultant to a new company which has developed a very promising method of disposing of solid waste. The process involves shredding, baling, and encapsulating. The material is highly compressed and encased in heavy sheet plastic which is shrunk-fit. The blocks of compressed material have a density greater than that of water, and can be buried in landfills or in water and collected for reprocessing at some later time. Additionally, these blocks can be used to reclaim certain islands that are washing away, provided that proper perimeter protection is provided against wave action.

PERSONAL ASIDE

What was the most satisfying assignment in your long and varied professional career? It has not been any single assignment. Rather it has been the satisfaction of working on many projects over the years, starting with modest jobs and in later years being associated with some of the very largest projects of their type. The Sydney water treatment project, which will be one of the world's largest, is an example. We were able to come up with a fairly unique plan, which is about to be carried out.

Starting way back in 1940, I was the firm's first cooperative-work student, while an undergraduate civil engineering student at Northeastern University. You might say that I have had an opportunity to grow with the firm, because we had less than a dozen people in those days.

Starting out in the planning stages of some of these more complex projects and seeing them develop is really a lot of fun. I'm one of those guys who regularly work extra hours evenings and weekends. But then I play hard too; last month I went big game hunting for ibex in the mountains of Iran. People sometimes ask me why I work so hard. I tell them, "Don't feel sorry for me; I love it. You should be so lucky!"



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Volumetric tests are conducted by titrations using a unique buret and titration stand. This device dispenses titration solution so that reliable results can be achieved from test to test. Enough of each reagent is supplied to run 100 average titrations.

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OUTLOOK

World-wide strategies for clean air rely heavily on the burning of low-sulfur residual fuel oil whose demand strongly points to the need for . . .

Desulfurization refinery capacities

In some places on the East Coast this past winter was the mildest in recent history. In others, it was the severest on record. In any case, the East Coast relies heavily on burning residual fuel for heating buildings and apartments and for operation of manufacturing industries and electric utilities. Clean air strategies along the East Coast rely primarily on the burning of low-sulfur fuel oil to meet clean air deadlines mandated by the Clean Air Act of 1970. Much of the fuel is low-sulfur residual fuel oil, and its availability is quite vague at this point. Desulfurization technology (i.e., removing sulfur from residual oil) is feasible but results in a significant cost increase for the "clean" fuel variety.

The public's attention to the supply and demand of low-sulfur fuel oil is focused none too early, at least considering these facts:

- the average annual increase for the demand of residual oil between 1970-1985 is projected to be 4.5%
- there has been a virtual stagnation in the growth of petroleum refinery capacity in the U.S. in relation to the U.S. demand for petroleum products
- over past years, U.S. refiners have maximized high-octane gasoline and distillate production, to the detriment of residual fuel production
- with the knowledge that it takes at least 2.0 to 2.5 years or longer to complete a refinery from contract to actual start-up, and with the position of the oil industry today, virtually nothing in terms of new capacity for low-sulfur residual fuel could be realized until sometime in 1976, after the mid-decade deadline for clean air.

Between now and 1976 the plaguing question is whether the supply of low-sulfur residual fuel will be available to meet the clean air deadline or will exceptions have to be granted? These questions simply cannot be answered at this time.

Of course, other fuels are burned to meet the clean air deadlines too. Natural gas is available on the West Coast, coming from Canada and Texas, and a certain amount will be available on the East Coast in accordance with the recent agreement to

import LNG from Algeria. But the main supply of natural gas for the East Coast comes from the Gulf Coast area; Canada doesn't plan to increase its exports to the U.S., and the Texas production is at capacity now.

What it is

Residual fuel oil is identified by two other terms—No. 6 fuel oil and Bunker "C." There are also No. 5 and No. 4 fuel oils (as the numbers decrease so too does the oil's viscosity); No. 4 contains an appreciable amount of distillate products. There is no No. 3. No. 2 is the light oil used for home heating, and No. 1 is kerosene which can be burned in home appliances.

Basically, there are two types of crude oil, sweet and sour. Sweet crudes are low in sulfur content, usually containing up to a maximum of 1% sulfur, and in general, most U.S. crudes are sweet. The sour crudes contain from 1-4% sulfur, and the object of desulfurization is to lower the sulfur content of the products obtained from sour crude to 1.0-0.3% sulfur.

Of course, the sweet crudes produced in the U.S. could be used to make low-sulfur residual fuel, and

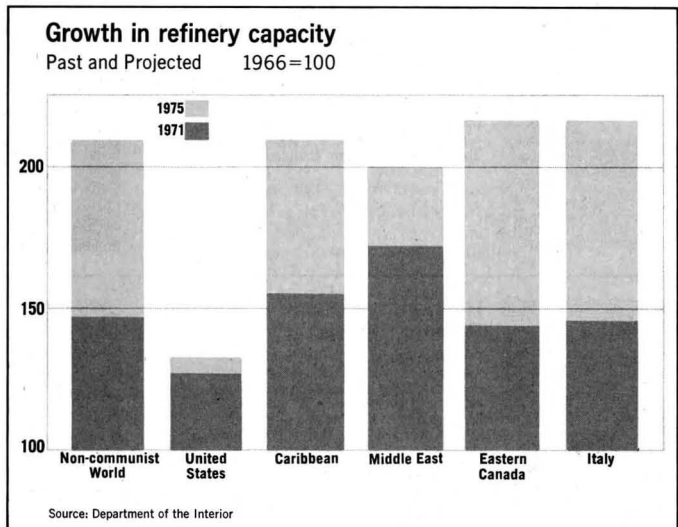
some are, although the supply is limited. But U.S. refiners have chosen to make coke and distillate fuel oil and naphtha as the products from their operations. The coke is used primarily to make anodes for the manufacture of aluminum. Naphtha, of course, winds up as gasoline; and after passing through a catalytic cracker, the distillate too can produce gasoline.

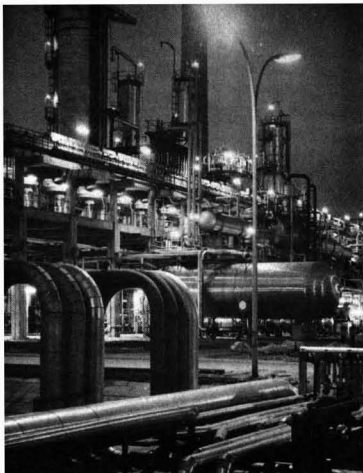
There is a growing concern for availability of low-sulfur residual oil. Some sources indicate that there soon will not be enough such fuel oil available and that certain exceptions will have to be granted to the clean air deadline of mid-1975.

The supply

In 1972, the supply of residual fuel oil in the U.S. was 925.6 million bbl; the supply is made up from U.S. producers, imports, and inventory changes. Official tabulations of the Department of the Interior Bureau of Mines reveal that in 1972 a total of 591.7 million bbl of residual fuel oil were imported into the U.S. In the same year, the U.S. produced 292.5 million bbl.

The big user of residual oil is the East Coast, or PAD-1 (Petroleum Administration District-1), an area ex-





New refinery. Two-2.5 years from contract to start-up

tending from Maine to Florida and including Pennsylvania and West Virginia. Various state and local air pollution control strategies require the burning of low-sulfur fuel oil, down to a minimum of 0.3% by weight, in high-density metropolitan areas such as New York City.

In 1972, 68.1 million bbl were used in PAD-1. (PAD-1 refineries produced 37.6 million bbl; most of the difference came from PAD-3, on the Gulf Coast.) In the same year, 99% of the imported oil was used in PAD-1. Incidentally, PAD-5, which includes California, is the next largest user of the residual oil produced in the U.S.

How to desulfurize

At present, many U.S. refineries have some capacity for removing sulfur from light and distillate oils but have little capacity for the production of low-sulfur residual fuel oil from sour crudes.

Low-sulfur residual fuel oil can be made from sour crudes by either a direct or indirect process. In the direct method, the heavy gas oil and residual are desulfurized at the same time. The indirect process splits the heavy gas-oil portion, desulfurizes it, and blends it back with the undesulfurized residual (see diagram). Sweet crudes are amenable to the direct desulfurization process or can produce low-sulfur residual directly without desulfurization. In fact, most of the U.S. production of low-sulfur residual oil is made from sweet crudes without any desulfurization process.

In the indirect process, the atmospheric residue is vacuum distilled to give a vacuum residual and a vacuum distillate. The distillate is passed through a hydrodesulfurizer which re-

moves the sulfur. The desulfurized distillate is then blended back with the vacuum residual.

The necessary catalyst is usually either a cobalt-molybdenum oxide or a palladium catalyst. However, some Arabian crudes can be desulfurized by the direct process also.

The sour crudes, especially those from Venezuela, contain nitrogen materials and high metals content—vanadium and nickel—which play havoc with the lifetime of the catalyst used in the desulfurization process. In general, Venezuelan crudes have high metals content; Middle Eastern crudes have medium metals content, and African crudes are low in metals. By vacuum distilling (the indirect route), heavy metals and nitrogenous materials are left in the residue.

Additional processes are being developed to recover sulfur—flue gas desulfurization, fuel gasification, fluid bed combustion. However, the lack of well-documented and publicly available information on these processes makes it difficult to judge their costs and technological merits.

Building

A number of well-known construction firms can handle the engineering and construction of desulfurization facilities—Badger, Bechtel, Fluor, Foster-Wheeler, Lummus, and Procon. A desulfurization plant costs on the order of \$50–100 million. But it is important to remember that only plants that either have been announced or are in fact under actual construction at this time can produce a low-sulfur residual fuel oil commodity by 1976.

Who they are

Two units—Texaco Trinidad and Exxon (Creole refinery at Amuay, Venezuela) go on stream this year; the Bahamas Oil refinery at Freeport, Grand Bahama, will go on stream later (see box).

All of the desulfurization facilities which serve the U.S. market are in the Caribbean with the exception of Shaheen's Isomax plant in Canada. In 1972, 92% of the U.S. imported low-sulfur fuel oil came from six countries—Bahamas, the Caribbean area, Italy, the Netherlands Antilles, Trinidad, and Venezuela. The remaining 8% came from several other countries.

Of course, many of the refineries were attracted to these six countries originally by the proximity to large producing fields and in some cases the practically limitless amounts of cheap natural gas for plant fuel. More recently, large refineries have begun to develop in the island areas where the location incentives include

circumvention of certain import quotas (which have recently been lifted), low taxes or tax exemptions, the availability of deep water unloading sites, and less stringent environmental requirements than in the U.S.

The installed and planned facilities in the Caribbean area use the indirect process for desulfurization. Perhaps, the newest desulfurization plant to go on stream is the Texaco Trinidad (a subsidiary of Texaco, Inc.) Point-a-Pierre refinery on the island of Trinidad, off the coast of Venezuela. The refinery's total capacity is 350,000 bbl/day, about 25% of which goes for the production of low-sulfur residual fuel oil (some 90,000 bbl/day).

Gulf's Bayamon refinery (San Juan, Puerto Rico) can produce 12,000–16,000 bbl/day of low-sulfur residual fuel oil. Its capacity for this commodity is not significant, how-

Process technology for desulfurization of crudes

Licensor	Process
Chevron	RDS Isomax
Cities Service/HRI	H-Oil
Essq-Union	Residfining
Gulf	HDS
Institut Francais du Petrole	IFP Resid
Standard Oil Co. (Ind.)	Resid Ultrafining
Universal Oil Products	RCD Isomax

ever. In this case, the residual is prepared by blending distillates with the residual (the refinery apparently desulfurizes light distillates).

Of course, the construction of other low-sulfur residual fuel plants have either been announced or are under way today. If on stream by 1975, then they may help alleviate the shortage of low-sulfur oil. Such expansion announcements include:

- by the end of 1973, the Canadian firm—Shaheen Natural Resources—plans a new refinery for Newfoundland & Refinery, Ltd. The throughput of the refinery is 100,000 bbl/day, and it has been estimated that some 35,000 bbl/day of low-sulfur residual fuel oil will be produced

- also by the end of this year, Creole, a subsidiary of Exxon, will expand its capacity by 50,000 bbl/day for the low-sulfur residual fuel oil commodity. Creole's refinery at Amuay, Venezuela, uses the indirect desulfurization process (referred to as the ERE process)

- another desulfurization plant

scheduled for start-up in 1973 is Bahamas Oil and Refining. Owned by New England Petroleum Co. and Standard Oil & Refining Co., it will expand its capacity from 250,000 bbl/day to 400,000 bbl/day. What percentage of this goes for low-sulfur residual fuel oil is unknown. In this case, the \$50 million expansion is being built by the Italian firm, SNAM Progetti

- also this year, Amerada-Hess in the Virgin Islands will expand its existing facility for the production of low-sulfur residual fuel oil

- another desulfurization plant is going into the Netherlands Antilles. Lago Oil and Transport (at Aruba, N.W.I.), a subsidiary of Exxon, plans to increase the capacity of its distillate hydrodesulfurization unit by 45,000 bbl/day by mid-1974

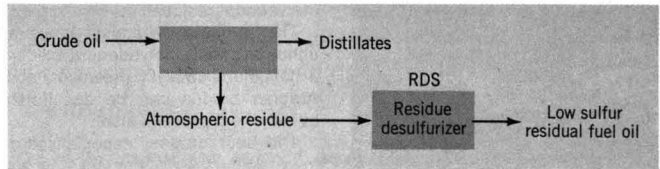
- by 1975, a new Virgin Islands HDS plant will come on stream. The Virgin Islands Refining Co. will produce low-sulfur residual fuel by an indirect process; this plant is currently under construction by Procon, a subsidiary of UOP

- Shaheen Natural Resources plans other desulfurization plants. A \$223 million refinery is to be built in Nova Scotia at Port Hawkesberry on the Strait of Conso. Although no contract had been let at press time, the plans included a 200,000-bbl/day refinery, of which 80,000 bbl/day would be low-sulfur residual fuel oil

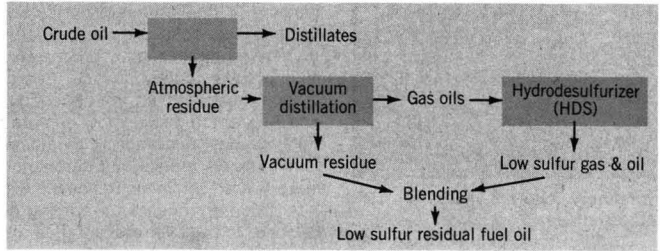
- Shaheen also plans a third refinery, but this refinery will not figure into the 1975 supply figure for the low-sulfur residual fuel oil commodity. A 300,000-bbl/day refinery will be built at Come by Chance, Newfoundland. Although the percentage of low-sulfur residual oil has not been revealed, there is press mention of use of the Isomax and Hydrobon processes, both of which are used for desulfurization

- there is also conjecture on other desulfurization plants. For example, Shell is building a new distil-

Direct desulfurization



Indirect desulfurization



lation plant in Curacao. Some sources say it's an additional refining facility; others say it's a replacement unit.

Foreign sources

Not only is the U.S. relying heavily on burning low-sulfur residual fuel to meet clean air strategies but so too are European countries. However, European sulfur fuel levels are projected to continue well above U.S. and Japanese standards with the exception of congested areas.

According to the CEC (Commission of the European Countries) report of December 1972, Japan is projected to be a big producer (and consumer) of low-sulfur residual fuel oil. According to this report, Japan will almost triple its production by the indirect desulfurization process and more than quadruple its production by the direct process. Prior to 1972, Japan produced 364,000 bbl/day by the indirect process but will be producing 911,000 bbl/day in 1975. Similarly, prior to 1972, Japanese

production by the direct route was 153,000 bbl/day which will increase to 645,000 bbl/day in 1975.

According to the Committee on Conservation of Air and Water, Western Europe, the published cost data for desulfurization only included the minimal cost, and the Committee concluded that the costs for adding desulfurization capacities were consistently higher than those usually quoted.

Foreign countries, including Australia, Belgium, Denmark, Finland, France, Germany, Greece/Italy, The Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom, have each considered placing limits on the sulfur contents of fuels, and some have already done so. All of which points to a European need for additional desulfurization capacities and the availability of low-sulfur residual fuel oil.

Only a few new facilities are known:

- in 1973, a Caltex company at Bahrain (in the Persian Gulf) plans to bring on stream a 50,000-bbl/day plant

- in 1972, Petroleos Mexicanos at Salamanco, Mexico, started up a 18,500-bbl/day desulfurization plant

- also in 1972, Shell/Koppartrans at Bothenburg, Sweden, brought on line a 2500 direct residual plant.

In the short term, the availability of the low-sulfur residual oil will not meet the onslaught of clean air strategies. New desulfurization plants will be an area for expansion by the oil industry. In the long term, new and additional desulfurization plants will be added, and this "clean" air fuel will cost significantly more than its source. The big question is whether clean air is worth the price. SSM

Fuel oil hydrodesulfurizer feed capacity

Company	Refinery	Capacity (thousand bbl/day)	
		Estimated 1972	Estimated 1975
Borco	(Bahamas)	0	60
Exxon	Creole-Lago (Amuay, Venezuela-Aruba)	200	300
Hess	Amerada (St. Croix, V.I.)	70	140
Shell	Cardon (Curacao)	60	60
Texaco	(Trinidad)	0	90
TOTAL		330	650

States' role in environmental protection

State governments are actively supporting environmental legislation, but officials question similar federal bills and the preemption authority involved

During 1972, legislatures in the 50 states passed some 129 bills into law that either regulate or otherwise pertain to environmental quality. The states are obviously concerned about protecting the environment and their role in doing such. In fact, a second National Symposium on State Environmental Legislation was held in Washington, D.C. recently. Sponsored by the Council of State Governments, EPA, and CEQ, it was attended by some 300 state and federal officials.

The attending delegates aimed to produce, after in-depth, intense discussion, model legislation that, with minor variations, could be adopted by any state to cover pertinent environmental issues and yet conform to federal requirements. The delegates covered nine major topics—water quality and the permit program, water quality and potable water, environmental facilities financing, noise control, state environmental policy act, land use and coastal zone protection, mined area protection, parks and wilderness areas, and endangered species and wildlife. Seven pieces of model laws were produced after much debate (sometimes heated) and information exchange in the various workshop sessions.

Model legislation completed

Here's how the states view the various environmental issues in question. The workshop on the water quality permit program expressed concern over the number of technical problems the 1972 Amendments to the Federal Water Pollution Control Act create for state legislators and environmental officials. However, the proposed legislation details issuance of permits, treatment guidelines, monitoring, permit modifications or suspensions, enforcement, and conflict of interest in pollution control board membership, although the bill is written to be broad to avoid conflict with federal programs.

The model bill on potable water quality is based on the assumption that the drinking water bills in Congress (S. 433 and H.R. 1057) will be enacted, with some modifications. The states' bill centers around the

philosophy that the states know best, and consequently, all controls in the bill are in the hands of state governments which would have little responsibility to the Federal Government other than adopting the federal standards for drinking water.

The model noise control bill, based on the Federal Noise Control Act of 1972, aims to give the states the widest power possible consistent with the preemption provisions of the federal act. It covers environmental noise, product noise, labeling, notice of noisiness in real estate transactions, and ambient, building, aircraft, and airport noise standards.

Based on the National Environmental Policy Act and California environmental impact guidelines, the proposed states' environmental policy act requires impact statements on proposed actions and mitigation measures to minimize environmental impact and growth aspects.

Geared to ensure minimal environmental impact from surface mining, the mined area protection bill covers state control of development, permit systems, selective prohibition, minimum reclamation, bond and forfeiture provisions, and citizen suits. The conference delegates were in favor of such state legislation rather than federal controls.

The parks and wilderness area workshop proposed a State Commission of Recreation to cover a state wildlands preservation system. Understandably, the system includes protecting recreational lands from transportation development, preser-

vation of selected rivers in their free-flowing state, road systems for access to scenic and other recreational attractions, and a trails system for outdoor recreation. The Committee on Endangered Species and Wildlife proposed three bills, dependent upon federal legislation, to cover endangered species and nongame conservation, effects of development on endangered species and nongame, and animal damage management.

Topics of unrest

The delegates discussing the financing of environmental facilities and land use did not present model bills. Since financing is handled in so many ways across the nation, the attendees agreed that no one piece of legislation could possibly be applicable to all states.

The workshop on land use and coastal zone management was perhaps the most popular, or controversial, of the sessions. The representatives agreed that the states need money and technical assistance for land use policies, but that the final power should lie within state jurisdiction. The delegates echoed Vermont's Governor Thomas Salmon's sentiments that "none of these (national land use policy) pieces of legislation will accomplish" the necessary goals. He urged "that the foundation for any land use legislation, be it state or national, must reflect administration and decision-making as close to home as possible."

The underlying current of the conference centered around the federal-state relationship. State officials complained about ever-changing federal requirements, and the issue of states' rights was continually debated and emphasized in the model bills. State Representative E. L. Henry of Louisiana emphasized that more concise information from the federal level is needed before state and local handling of environmental problems can be tackled. He termed written instructions "gobbledygook" and asked "What the devil are the federal programs?"

Representative Henry cited cases where, written instructions not being available or intelligible, state officials receive "verbal instructions" on complying with federal regulations. However, after following those instructions and later being told by the federal agency that they had "misinterpreted" the instructions, some of the state agencies are now tape-recording their conversations with federal agencies. Airing intergovernmental relationship problems and difficulties of drafting "model" legislation may be the first step in solving the same. CKL

Louisiana Rep. Henry
Instructions are "gobbledygook"



Trade consequences of environment cleanup

Federal antipollution laws will place U.S. industries competing abroad at a disadvantage unless foreign countries are required to pay fair shares of their own pollution abatement programs

Present federal antipollution laws will cause "significant economic consequences" for U.S. industry competing abroad unless firms in foreign countries are required to pay fair shares of their own pollution abatement programs. Although more cost data are needed before the full impact of these regulations is known, pollution control laws will affect the "profitability and viability of particular firms and industries." These conclusions were reached in a recent Department of Commerce report on the international trade effects of U.S. antipollution controls. The study is the first of a series of annual reports mandated under Section 6 of the Water Pollution Control Act amendments of 1972.

Paul O'Day, deputy director of Commerce's Bureau of Competitive Assessment and Business Policy, who supervised the study, told *ES&T* that the unavailability of cost information created definite problems in preparing the report. He pointed out, however, that an overall picture of what U.S. industry faces does emerge, and that the report is useful because of this overview. In illustrating the data handicap, he said that the findings of a joint report by CEQ, EPA, and Commerce in 1971, and an EPA study in 1972, were useful, but that these earlier reports were based upon projections of pollution control standards that are now largely out of date. He said these earlier studies covered only capital investments and direct operating costs, not indirect costs such as those imposed on suppliers.

According to Richard Puz, the Commerce employee who directed the study, "Data were particularly lacking when we moved abroad." He told *ES&T*, "I see the report, because of the lack of specific cost data, mostly as a starting point." He said, however, the report does provide useful information. He pointed out it reviews the pollution controls required by the U.S. and nine countries directly in competition with U.S. industry, and that it demonstrates how costs, when finally available, can be traced through the entire infrastructure of a particular industry to provide figures that can be compared.

In focusing upon Belgium, Canada, France, Germany, Italy, Japan, the Netherlands, Sweden, and the United Kingdom, the report considers countries that in 1971 represented 58% of total U.S. merchandise exports and 65% of total merchandise imports. If this ratio were thrown further out of balance because of competitive disadvantages imposed upon U.S. industries, serious political, as well as economic, consequences could result. It was for this reason that Congress directed the Commerce Department to undertake the study.

The report finds that foreign competitive advantages could result from two facts: lower foreign levels of pollution control and foreign government actions that subsidize industrial compliance. It points out that in the U.S., amortization of the entire cost of equipment over five years is permitted, but that industry is forced to use straight-line depreciation because the investment tax credit does not apply. As to the pollution control laws in foreign countries, they were found to vary from comprehensive to non-existent.

Foreign pollution laws

In Belgium, comprehensive laws have been enacted. In addition, new

water pollution regulations are to be issued there this year, and air pollution standards for industrial and power-generating plants are under study. An existing law requires that all fuel oils produced and used for domestic heating after August 5, 1973, must have no more than 1.0% sulfur.

Canada has comprehensive legislation in the field of water resources. When fully implemented, its law will rely on regional water resource management agencies to control all aspects of water use, including the setting of environmental water quality and discharge standards. Also, national effluent discharge limits have been set by the national government there for the pulp and paper industry, and similar standards are being developed for several other industries. Strict air pollution regulations, however, can be found only in the province of Ontario, as the less industrialized provinces have done little to curb industrial air pollution. The law provides that air quality standards be set by the provincial governments, which must take into consideration national air quality objectives.

France has established laws for surveying and controlling pollution in its rivers, and the power of water management agencies there is being strengthened. Its air quality laws are less stringent; however, authorities

Depreciation allowances for pollution control equipment

Country	Percentage and time	Comments
Canada	100% in 2 years	Equipment purchased 1965-73
France	50% in 1 year	Facilities built 1968-74; in addition to normal accelerated depreciation
Germany	50% in 5 years	In addition to straight-line depreciation
Italy	None	...
Japan	50% in 1 year	In addition to accelerated depreciation
Sweden	None	...
United Kingdom	None	...
United States	100% in 5 years	Equipment purchased after 1970 for plants built before 1969; 5-year period must be amortized on straight-line basis; no investment tax credit permitted

may impose conditions regarding the quality and content of gaseous emissions into the air prior to the construction of an industrial plant. Although standards are rigorously enforced in nationalized industries and utilities, they are not strictly enforced with respect to private firms.

Air and water pollution standards in Germany vary widely, since its federal government may recommend emission and discharge standards but must rely on the states to adopt and to enforce them. But the situation there could improve dramatically as constitutional amendments to centralized environmental control authority and ambitious federal legislative proposals to control air and water quality are now under way.

In Italy there is only minimum control of pollution, and the development and enforcement of standards vary from region to region. The country has no water pollution legislation at all, but it does have a 1972 air pollution law that provides for emission standards regulating heating installations, industrial plants, and motor vehicles.

Japan recently has demonstrated great interest in its environmental problems, enacting 14 new laws that provide for comprehensive controls of air and water pollution. Whether and to what extent these laws will be effective in abating that country's serious pollution problems, however, must await their implementation and enforcement.

The Netherlands has a comprehensive water pollution abatement program and a comprehensive air pollution program under development. Its water pollution control program, which is similar to the U.S.'s, prohibits the discharge of effluents into surface water without a permit and specifies what water quality or discharge standards must be met. Its air pollution is controlled by emission standards placed on manufacturing and service plants. To assist in the enforcement of these standards, a nationwide network of 250 monitoring stations and 10 regional measuring centers is being constructed.

In Sweden, a special license is required of firms using specified production processes that may result in air or water pollution. The license, which is legally enforceable, sets up for each project the operating conditions and standards the firm must follow. The terms of each license are negotiated with the government and follow national recommended standards. They take into consideration the economic ability of the firm to meet the recommended standards; however, the burden of proof lies with the firm if it believes it is unable to meet such standards.



Paul O'Day
Supervised study

Local and regional authorities in the United Kingdom set and enforce emission standards on a case-by-case basis. In theory they apply a "best practicable means" standard in determining the extent to which a firm is technically and economically capable of meeting the established standards. While enforcement is not consistent, significant progress has been made in abating smoke, grit, and dust emissions. As to water discharges, approval must be obtained from river authorities. Their responsibilities include the determination of effluent standards for new and existing sources as well as the conservation, redistribution, and augmentation of water resources.

Cost considerations

Pointing out that U.S. industry will face competitive disadvantages in regard to these nine countries is one thing; determining the extent of these disadvantages is a more complicated matter. The problem is one of cost methodology, and a variety of factors need to be looked at, according to the report. For one thing, consideration must be given to the "combined" impact of pollution control requirements upon firms and their suppliers. Whether glass, plastics, or steel industries are studied, prices have to be accumulated in the end product—the automobile, the appliance, or the building material—before their full impact on international markets can be known.

The report adds that additional data collection problems arise because of the size and competitive natures of some companies. Multidivision or multiproduct companies present situations that complicate the determination of actual costs on a product basis. In addition, the pro-

Richard Puz
Directed study



proprietary nature of information on production costs, and their implications for an industry's competitive position, will not permit some companies to make detailed information available.

The report finds that the translation of production costs into actual market prices is equally difficult in that it involves not only the assessment of likely incremental financial returns but also premises regarding the performance and service standards of the market. Customary profit margins, the target return on investment, and the return on equity sought by individual firms, all must be considered since the structure of an industry and the quality of competition are major influences on pricing. Intercompany and interindustry variations in these areas will further complicate the matter.

Finally, pollution-related material and labor inputs must be traced throughout the entire industrial infrastructure, if indirect costs are to be determined fully. And this should be accompanied by statistical analyses of possible errors so that the final result will yield a set of average values for cost and price effects rather than point estimates. Although the use of input-output tables may be feasible, this requires correct assumptions regarding price elasticity, shifts in markets due to substitutability, and other factors before final prices can be determined. The report notes that price results can be in error when projected through a variable such as time, unless changing cost figures are taken into account.

The magnitude of these methodological problems is large, but it will diminish to some extent as the cost effects of pollution control gradually become known. Thus, the general level of these cost impacts will be easier to identify after we have lived with them for a while.

But what good will the working out of these involved cost problems do if, finally, the U.S. is unable to compete with foreign firms that are not required to pay their own pollution abatement costs? The report finds hope in the Organization for Economic Cooperation Development (OECD) adoption, in May 1972, of the "polluter-pays" principle whereby the 23-country body agreed that antipollution costs should be born by the producers. This is the "harmonization" President Nixon supported in his 1973 State of the Union address when he affirmed that "the costs of pollution should be more fully met in the market place, not in the federal budget." Whether this will be internationally adopted by the late 70's when U.S. antipollution laws are fully in effect, however, remains to be seen.

WSF

Industry looks at water reuse

National Conference on Complete WaterReuse
outlines problems and prospects for industry

Look for reuse of waste water to become more commonplace in industry as discharge limits move inexorably toward the zero mark by 1985. That was the consensus of opinion at the recently convened National Conference on WaterReuse, sponsored jointly by the Environmental Protection Agency and the American Institute of Chemical Engineers.

Public Law 92-500, better known as the Federal Water Pollution Control Act Amendments of 1972, is putting the screws to polluters. The national goal of achieving zero discharge of water pollutants by 1985 is making industry take a fresh look at reuse. More often than not, the conclusion will be that it's cheaper to treat for reuse than to treat for discharge.

Costs and benefits

The decision on treat or reuse, like so many others in pollution control, must be made with regard to both the costs and benefits of the proposed plan of action, according to Lawrence Cecil, a Tucson, Ariz., chemical engineering consultant who chaired the conference. While many industries "use" large quantities of water, the basic concept of water use is that water is "borrowed" instead of "consumed," pointed out E. D. Dyke, of E. D. Dyke and Sons, Ltd., Ashford, England.

Only a few industries incorporate sizable quantities of water into their products—industries such as food processing, ice manufacture, and the like—while most others simply use the properties of water to attain their purposes. "Complete cycle stream to stream is the ideal; a closed cycle cannot be closed absolutely," Dyke pointed out. He told conference attendees that consideration must be given to the enlarged cycles, taking into account oceans and atmosphere, and said that due weight must be given to "rights and liabilities at point of access," to water supplies.

In addition to economic discussions of the costs and benefits of

zero discharge and water reuse, there were discussions of the various technologies available for reusing water and case histories of successful operations. In the forefront of available technologies are reverse osmosis, activated carbon adsorption, continuous ion exchange, and eutectic freezing processes. Such techniques, while they may not remove every last trace of pollutants, produce water of sufficiently high quality that it can be recycled or reused.

Several participants pointed out the distinction between recycling and reuse, where the former refers to using treated water in the same application for which it was previously used, while reuse could include other applications where water quality was less critical. Still other discussions centered around reclaiming incidental contaminants, including low-level waste heat, for productive use.

Medium sized lumber mills, for example, have a tough time disposing of wood wastes, Don White of the

University of Arizona, Tucson, told the conferees. A conceptual study shows that a possible solution would be to hydrolyze the wastes with acids and ferment the sugars, turning the waste into a high-protein feed. Water would be reused in the system so that no liquid wastes would leave the process stream, White reported.

Using heat

The use of low-level waste heat has been receiving considerable attention from the Tennessee Valley Authority, according to TVA's C. D. Madewell. Projects under investigation include using waste heat from steam plants to heat and cool greenhouses, livestock, and poultry housing; subsoil heating to increase the growing seasons of certain crops; and enhancing catfish production in raceways.

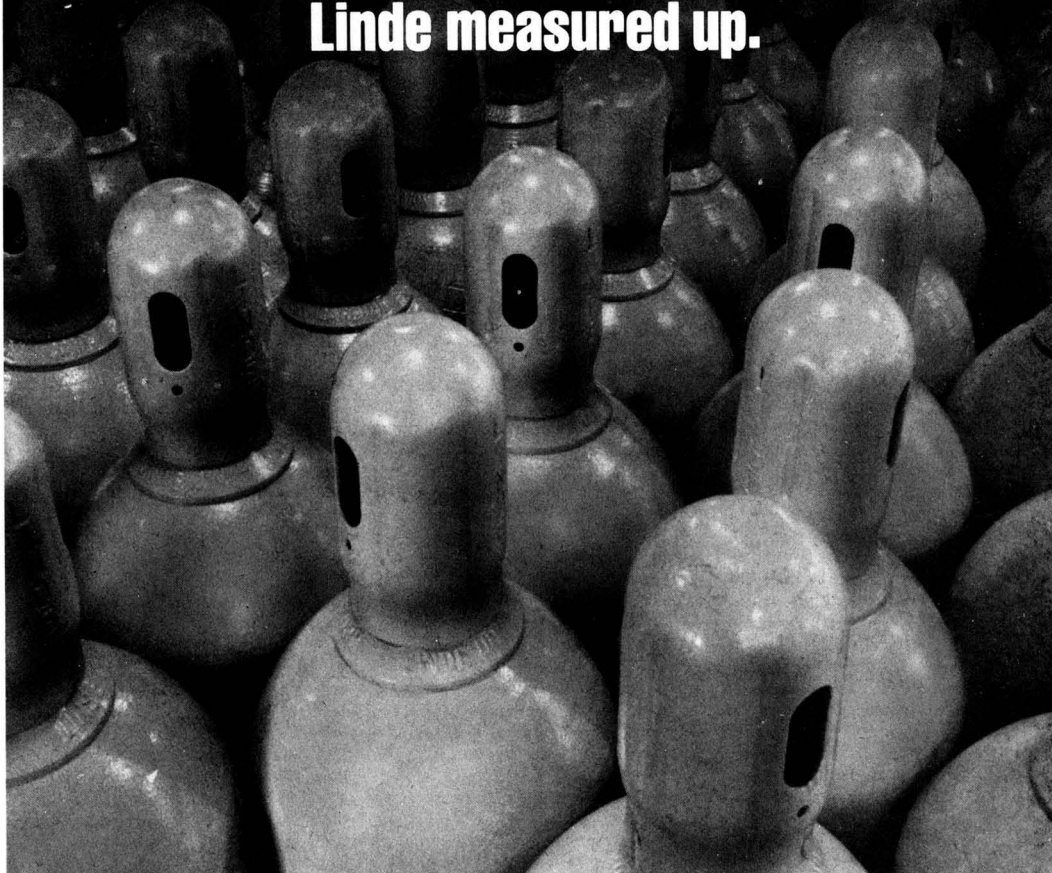
Several symposium participants pointed out that secondary municipal sewage plant effluent could be used to augment cooling water make-up requirements for power-generating plants. R. A. Sierka of the University of Arizona went the other way in describing uses of waste heat from nuclear power plants to augment a physical-chemical sewage treatment system. Such a combination power plant-sewage plant would use each other's wastes in a form of industrial symbiosis.

L. J. Boler of Cherne Industrial, Inc. (Edina, Minn.), proposed a similar solution using waste heat from a 1000-MW generating plant to enhance operation of an extended aeration biological sewage treatment plant. The two plants in tandem could take care of the power and sewage treatment requirements of a city of 1 million people. The benefits: reducing need for fresh water to cool the power plant by using sewage as a coolant, trapping waste heat for useful purposes rather than merely dissipating it, and reducing the horsepower necessary for handling both heat rejection from the power plant and introduction of oxygen into the sewage treatment plant. HMM



Lawrence K. Cecil
Chairs meeting

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Uv cure cuts pollution, energy use

Printing inks cured by ultraviolet light instead of heat promise to clear up emissions headache and conserve energy

Air pollution regulations are making inroads everywhere, and the printshop is no exception. Solvents from printing inks are coming increasingly under the gun from state and local regulatory officials as well as federal OSHA inspectors.

Solvents used in printing inks are volatile hydrocarbons. They must dry slowly enough to let the printer complete his job, yet they must dry rapidly enough to prevent smearing on today's high-speed presses.

A new breed of inks which cure by exposure to ultraviolet (uv) light promises to make hazardous solvent emissions in printing plants a thing of the past. Curing is done in milliseconds, an order of magnitude faster than that achieved with conventional heat-set inks. As an added bonus to their pollution abatement potential, uv inks drastically cut energy requirements for curing.

Conventional printing inks contain anywhere from 25-75% solvents—mostly esters and ketones—depending upon their applications. In conventional curing processes, these solvents are boiled away at temperatures exceeding 300°F by natural gas-fed dryers.

Increasingly tough air pollution control regulations are forcing printers to destroy those emitted solvents. That's most often done by activated carbon adsorption or direct fume incineration.

While both techniques work, burning the solvents takes additional fuel, usually natural gas which is already in critically short supply. Carbon regeneration processes require temperatures in the neighborhood of 500°F, again upping fuel costs. Furthermore, solvent recovery is made difficult by the oils, tars, and conditioners present in printing inks. On the other hand, ultraviolet curing takes place at room temperature.

How it works

Printing inks are formulated from monomers or oligomers which will polymerize when exposed to light. In addition to the monomers (typically esters of acrylic acids), conventional pigments are incorporated into the formula, as are scavengers, conditioners, and a photoinitiator such as benzophenone.

Printing is done in the conventional manner but instead of heat drying, the wet page passes under a lamp

assembly which irradiates the ink. The photoinitiator traps quanta of energy and is boosted to a triplet energy state. Decay from the triplet state is relatively slow (10^{-3} to 10^{-2} sec) and takes place by cascading which allows useful work to be harnessed for the polymerization reaction.

The monomers would trap some uv energy without the photoinitiator, but decay from the excited singlet or doublet state of the monomers is so rapid (on the order of 10^{-9} sec) that the ink would fluoresce instead of polymerizing.

The ultraviolet curing assemblies can be placed between units of the press or at the end of the press, depending upon space requirements and the type of printing being done. The inks are stable to the types and amounts of light usually found in printshops.

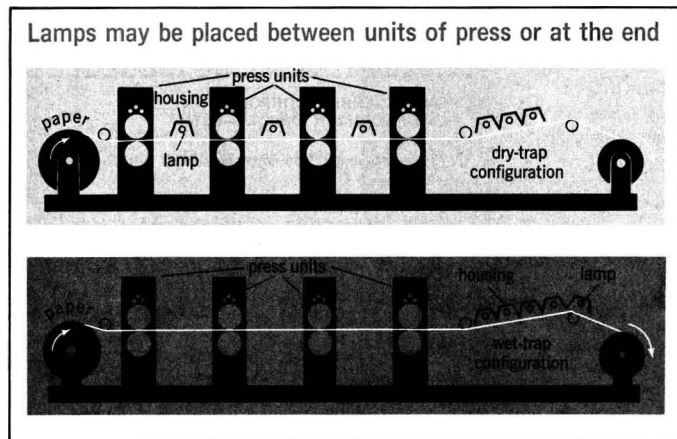
Economics

The primary drawback with inks at the present time is price. Conventional heat-set inks in basic black cost as little as a nickel per pound; however, uv inks cost about \$1.50 per pound. But the price differential is more apparent than real.

The cheapest inks will continue to be used in daily newspaper applications, where porous paper and mass production make them acceptable, says Gary Winters, director of market planning for Inmont Chemical Corp. (Inmont and Sun Chemical, New York, N.Y., are the two major manufacturers of uv inks.) But for applications requiring higher quality—packaging, label printing, magazines, and the like—the inks are already roughly competitive.

Energy use is a critical factor in the economics of uv inks for printing, explains Bohdan Burachinsky, Inmont's vice-president for research and development. The energy consumed by the curing process is only 25% of that consumed by conventional heat-set printing. With heat-set inks, it's necessary to heat the paper, and only 20-25% of the energy put into the system is actually used to dry the ink, Burachinsky says. Some 70-75% of it remains as heat in the paper. Furthermore, that 70-75% must be removed by cooling after curing which makes more demands upon scarce energy resources. Add to that the costs of incinerating, and the price of energy required for heat-set printing becomes substantial, Burachinsky points out. The lower temperatures also offer printers a savings on paper, since cheaper paper, which does not have to stand up under heat, can be used.

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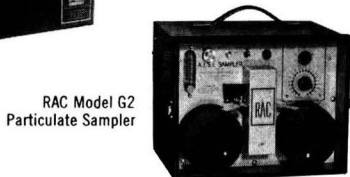
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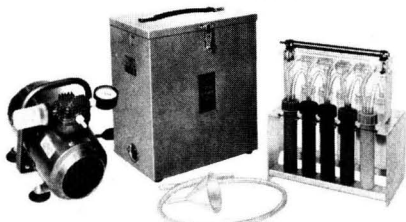
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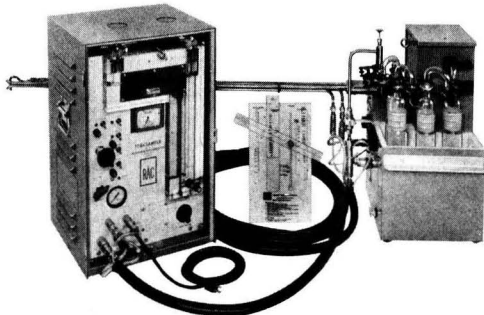
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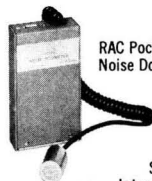
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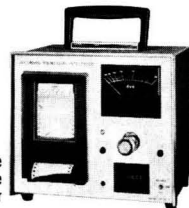
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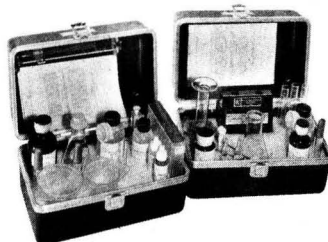
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FEATURE

Odor controls for rendering plants

Methods for curbing odorous emissions are used with varying degrees of success; without controls, rendering plant odors can be discernible at distances up to 20 miles from the source

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Rendering plants produce a variety of odorous emissions, depending on the types of raw material and process equipment used. Although both batch and continuous rendering processes are in use, the latter are becoming more popular for economic reasons, especially for new installations. Modern continuous rendering plants generally emit less odor than established installations because they feature enclosed material handling systems. In addition, odor abatement equipment is frequently an integral part of the total plant package.

Without controls, rendering plant odors have been reported discernible at distances up to 20 miles from the source. Unfavorable atmospheric conditions serve to magnify the problem so that a serious public nuisance develops, as evidenced by the number of complaints received by air pollution control offices both in the U.S. and abroad.

As of January 1969, there were about 850 domestic rendering plants owned by some 772 firms (Table 1). Approximately 460 of the total were operated by independent animal renders, 330 were controlled by the meat packing and poultry dressing industries, and the remaining 60 were owned by concerns with a variety of other interests. Some 275 of the plants controlled by meat packers also produce edible rendering products in separate locations at the same plant. There were 93 plants processing fish products and 11 feather mills not included in the above totals drawn from the most recent data available.

It is estimated that 20 new rendering plants will be installed in the U.S. each year. Virtually all will be replacement plants, and most will probably be of the continuous process type rather than of the older batch process technology.

All rendering plants, inedible grease and tallow producing works, and manufacturers and processors of animal and fish oil and by-product meal are in standard industrial classification (SIC) 2094. Processing of poultry wastes, including feather drying, logically falls in this category. Meat packing plants and captive or contract slaughtering houses (small game, on-premises canning and curing, and sausage and lard production excluded) are in SIC 2011. Although this includes abattoirs, blood meal production, and by-product hides, its primary group is food for human consumption and prepared feeds for animals and poultry.

The U.S. Environmental Protection Agency (EPA) is considering the development of standards of performance for new rendering plants in compliance with the Clean Air Act of 1970. The Act requires any control regulations to represent the best demonstrated technology, taking costs into consideration. One of the probable standards would be to limit the concentration of undiluted odors emitted from certain process equipment in any new or substantially modified rendering plant to no more than 200 odor units per standard cubic foot (ou/scf). An odor unit is defined as the quantity of any single odorous substance or a combination of substances which, when completely dispersed in 1 ft³ of odor-free air, is detectable by a median number of observers in a panel of eight or more persons. The odor concentration is determined by a modification of the ASTM D1391-57 observer panel technique which, in its present form, allows optional approaches to sampling and dilution.

A standard of 200 ou/scf allows for increased odor levels which may result from substitution of distillate fuel oil when natural gas is unavailable for firing afterburners. Odor levels from oil combustion are usually slightly greater than those from burning natural gas. Because odor strength is so intrinsically related to the olfactory sensitivity of the "smeller," it is difficult to define the intensity of the proposed standard for any single individual. The vari-

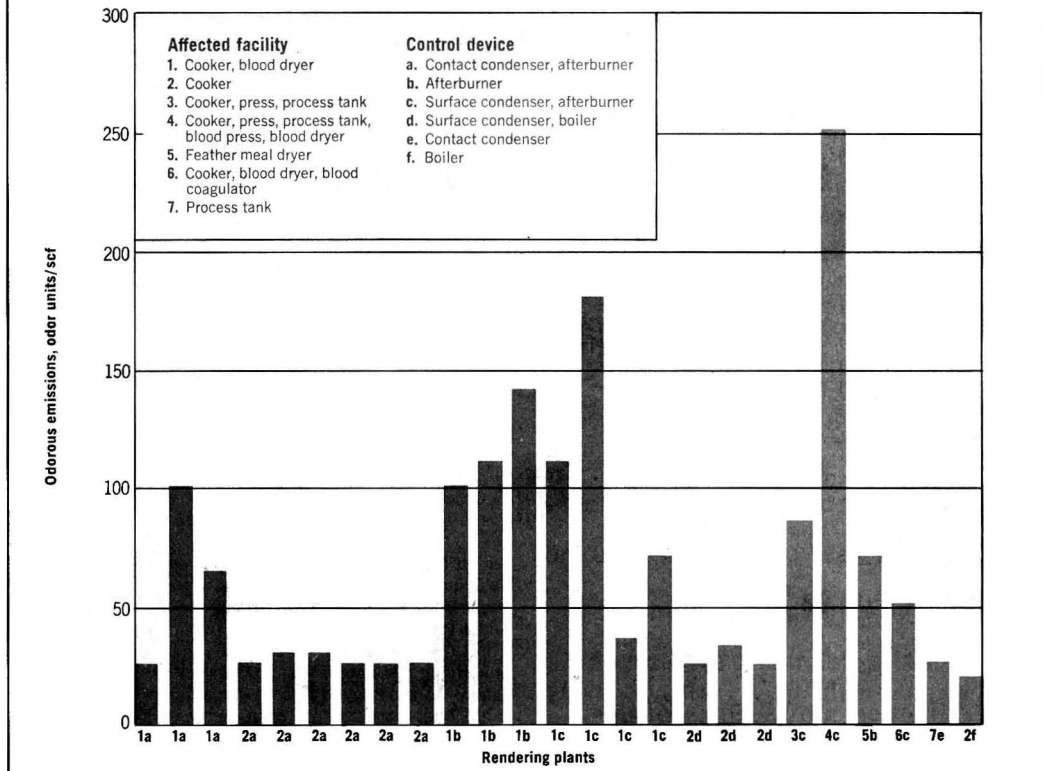
TABLE 1.
Rendering operators in United States

State	Independent renderers	Livestock slaughter renderers	Poultry slaughter renderers	Marine renderers	Feathermill	Blender
Ala.	11 (6) ^a	12 (6)	2 (2)			
Ariz.	5 (1)	1				
Ark.	5 (2)	3	6 (6)			
Calif.	32 (15)	11 (3)	1	8 (3)	4 (4)	
Colo.	5 (3)	9 (5)				
Conn.	2 (1)		1 (1)			
Del.	1					
Fla.	7 (4)	6 (4)	1 (1)	7 (4)		
Ga.	9 (6)	14 (9)	4 (4)	1		3 (1)
Idaho	4 (2)	4 (4)			1 (1)	
Ill.	21 (16)	17 (8)				4 (2)
Ind.	15 (13)	11 (7)				
Iowa	21 (14)	29 (12)		1 (1)		
Kan.	7 (3)	2 (1)				1 (1)
Ky.	4 (3)	9 (3)				
La.	5 (2)	7 (4)	2 (2)	33 (33)		
Maine	1 (1)		3 (1)	4 (4)		
Md.	8 (6)	2	1 (1)	2 (2)		
Mass.	5 (4)			2 (1)		1 (1)
Mich.	8 (4)	6 (4)				
Minn.	15 (13)	12 (5)				
Miss.	5 (2)	9 (6)	5 (5)	3 (3)		
Mo.	14 (5)	17 (7)	2 (2)			
Mont.	4 (3)	9 (3)				
Neb.	8 (6)	3 (1)				
Nev.	2 (1)	1 (1)				
N.H.		1				
N.J.	10 (5)	4 (2)		3 (3)		1
N.M.	2 (1)	4 (2)				
N.Y.	8 (3)	5 (1)		2 (2)		
N.C.	7 (4)					
N.D.	3 (2)	2 (2)	2	2		
Ohio	14 (8)	11 (4)			1 (1)	1
Okla.	5 (2)	11 (6)				
Ore.	6 (3)	6 (2)		1 (1)	1	
Pa.	37 (27)	12 (6)	2 (2)			
R.I.	5 (5)					
S.C.	6 (4)		1 (1)			
S.D.	3 (2)	6 (3)				
Tenn.	7 (3)	18 (6)				1
Tex.	17 (6)	37 (4)	2	1 (1)		
Utah	4 (2)	4 (2)			2 (2)	
Va.	5	6 (2)	1 (1)	11 (8)		
Wash.	10 (5)	11 (6)		7 (5)		
W. Va.			1 (1)			
Wis.	11 (7)	12 (8)		1 (1)	2 (2)	1
Wyo.	2 (2)	2 (1)				
Alaska	1			1		
Hawaii	2 (1)					
P.R.				3		
TOTALS	389 (228)	346 (150)	37 (30)	93 (72)	11 (10)	13 (5)

^a Numbers in () are installations in towns below 25,000 population.

FIGURE 1.

Odorous emissions from various rendering plants (Los Angeles Air Pollution Control District)



ation in sensitivity from person to person, although partially compensated by the use of a comparatively large panel in the test method, results in wide confidence limits in the test results. However, it would be reasonable to expect an odor concentration of 200 odor units from a rendering plant to be noticeable to most people. Coffee roasting or bread baking odors, with which the reader may be familiar, emanate at about 2000 ou/scf. In comparison, combustion of natural gas produces an odor level which has been measured at an average of 25 ou/scf.

The effect at ground level after atmospheric dilution of stack emissions of 200 odor units is less easy to define. By atmospheric dilution formula, the distance from the stack to the point at which the typical smeller would no longer detect an odor from the affected facilities can be estimated. Assuming the worst possible circumstances, the minimum distance would be less than 1000 ft from a typical rendering plant which incinerates 500-1500 scfm. This estimate does not allow for the contribution of odors from other sources in the plant which should be controlled by good housekeeping, covering or enclosing feedstock areas, and treatment of plant ventilation air.

Incinerator stack gas results from Los Angeles (Calif.) area were used as a data base. The standard, however, does not require the use of any specific odor abatement method. Tests by the Los Angeles Air Pollution Control District, averaging 67 ou/scf (Figure 1), reveal the following emissions when controlled by:

- A contact condenser-afterburner system
 - 3 plants with cookers and blood dryers, avg 63 ou/scf

- 6 plants with cookers, avg 27 ou/scf
- Surface condenser-afterburner system
 - 4 plants with cookers and blood dryers, avg 99 ou/scf
 - 3 plants with cookers using boiler afterburner (appreciable dilution in boiler), avg 27 ou/scf
 - 1 plant with cooker, press, and processing tank, avg 85 ou/scf
- Eight combinations of various control devices used on process equipment. Seven support the standard, and all eight average about 96 ou/scf.

Data indicate that odors from specified facilities can be held below the probable standard only if incineration is employed. In almost all cases, combinations of incineration and condensation reduced emission concentrations to less than 100 odor units. The combination is usually more economical as well as more effective because of the 20-fold reduction in gas volume which must be incinerated. With combination systems, an odor level of 200 ou/scf usually can be achieved at an incineration temperature of 1200°F. When no condensers are employed, it may be necessary to operate the afterburner at 1400-1600°F to achieve the required odor abatement.

EPA has not yet established air quality criteria for odors. The provisions of the Clean Air Act require that states develop regulations for control of odorous emissions from all existing rendering plant facilities covered under any federal new rendering plant performance standards.

The agency may be expected to suggest minimum odor control criteria to the states, probably under the new source performance standards. These standards will, of

course, apply uniformly to all new rendering plants. The states will then set their own standards which may be more stringent than those recommended by EPA; the states will set their own control requirements for existing rendering operations.

Poultry rendering emissions are predominantly aldehydes and small amounts of dialkyl disulfides. The odors associated with dry rendering of dead stock, beef offal, slaughterhouse trimmings, to name a few, all contain a variety of carbonyl compounds with traces of sulfurous and nitrogenous compounds. Fish meal processing produces mainly amino compounds from trimethyl amine to putrescine. In nearly all cases, the odors are accompanied by particulate matter and fatty mists.

Odor control systems commonly used at this time are condensation followed by incineration, or scrubbing, or a combination of these. Incineration has been the most effective method to date, especially for low-volume, high-concentration odors. Recent advances in the design and utilization of scrubber systems have significantly increased their odor-destroying ability until they nearly equal the performance of incinerators. Scrubbers are especially useful in controlling high-volume, low-concentration odors. The renderer frequently uses both systems for full plant control of all odors.

Other odor control methods, used with varying degrees of success by the renderer, include catalytic combustion, adsorption, and ozonation. However, no odor control system can be truly effective unless general cleanliness, housekeeping, raw materials handling and storage, and spill prevention throughout the rendering plant are properly managed by the operator.

Odor control by incineration

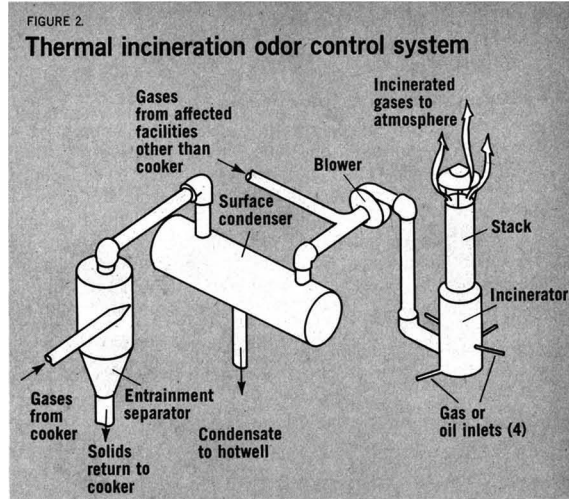
Combustion or thermal incineration is the most effective technique for controlling high-concentration odors in low volumes of air. The economics of this technique are enhanced if the odoriferous materials provide a significant fuel source. Unfortunately, rendering off-gas has no appreciable fuel value. Careful design is necessary to achieve complete oxidation of these gases. Otherwise, the partial oxidation products may be more odoriferous than the original pollutants.

Many renderers in Los Angeles County have used thermal incineration for more than 10 years (Figure 2). The malodorous gases emanating from tallow presses, processing tanks, dryers, and related equipment have also been controlled by thermal incineration.

Carefully designed hoods and ducting systems are used to minimize entrainment of ambient air and fuel costs. Some renderers duct the low-volume, high-concentration odoriferous emissions to the boiler firebox where they are burned. This method is attractive since no additional fuel is required to destroy the odors. Users of this method, however, have found that the incineration system must be well designed and constructed to prevent both odor blowback and corrosion of the boiler tubes. In addition, provisions should be maintained to control the odoriferous emissions when the boiler is at "low fire" during slack periods of plant operation.

The volume of odorous gases to be incinerated (following any condensation for fatty particulate matter removal) ranges from 500-5000 cfm, depending on the size of the plant and the material being processed. A large plant rendering chiefly beef scrap and bone may incinerate about 2000 cfm while a smaller plant processing feathers may handle about 5000 cfm. Waste heat recovery equipment may be used in the latter case to reduce odor control costs. Such equipment is commonly used to preheat dryer air or to generate steam.

EPA has calculated the cost of odor control for typical new and existing rendering plants which use the conden-



sation-incineration technique. Table 2 summarizes these control costs, which include capital investment and operating costs of the abatement equipment required.

Feather cooking and subsequent drying in the rendering process generate large quantities of acrolein, acetaldehyde, methyl mercaptan, diethylamine, *n*-propylamine, ammonia, and hydrogen sulfide. Pyrolysis of the off-gases effectively controls odor. Reactive scrubbing with 2,4-dinitrophenylhydrazine is a second-best choice based on the economics of rendering operations.

If a renderer desired to incinerate all of his process and ventilation air, the costs would be excessive. For example, direct flame incineration of 100,000 cfm of air containing 5 ppm of 1-butanol would cost \$1.15/hr/1000 cfm, without heat recovery. Also the costs would drop to \$0.77/hr/1000 cfm if half of the waste heat were recovered and if the odor-laden gases in both cases contained no fuel value. With no waste heat recovery, the operating

TABLE 2
Control costs for typical rendering plants

Plant type	Continuous (new) 7500 lb/hr product	Batch-1 cooker (existing) 780 lb/hr product	Batch-3 cookers (existing) 2600 lb/hr product
Emission control	200 ou/scf	200 ou/scf	200 ou/scf
Required control equipment	Surface condenser cooling tower incinerator	Contact condenser incinerator	Surface condenser cooling tower incinerator
Production, T/yr	12,000	835	4,160
Control investment, \$	43,000	6,050	35,200
Annualized control cost, \$/year	12,000	2,460	8,900
Annual cost per unit of product, \$/ton	1.00	2.95	2.10

Major assumptions: All control equipment depreciated over 20-year (straight-line) life. Product yield, 50% tallow, 50% protein meal.

cost of direct-flame afterburners for controlling rendering plant odors was \$0.64/hr/1000 cfm. However, this amount could be decreased to \$0.27/hr/1000 cfm with proper heat exchange equipment.

Odor control by catalytic oxidation

Catalytic oxidation has the advantage of operating at lower temperatures and thus with a lower fuel cost than thermal incineration, but neither process is economical for heating large volumes of essentially zero Btu of air. In addition, catalytic oxidation requires a suitable catalyst which will be unaffected by either particulate matter or sulfur compounds. For efficient and economical control of odors by incineration, odor sources should be isolated; their emissions should be treated separately and not mixed with ventilation air.

Catalytic oxidation has not become popular in the rendering industry despite the obvious advantage of using

insoluble in water. Even if a suitable universally effective scrubbing solution could be found, the odor would merely be concentrated in the liquid phase and thus become a potential water pollution problem. Odor removal by wet scrubbing is a function of the residence time of the odor-laden air in the scrubber, the available contact area, the solubility of the odorant in the water, and the concentration of the odor in the inlet gas stream.

Reactive scrubbing, as all types of chemical removal, requires that the contacting operation either yield inert precipitates upon reaction or form easily removable, nonodorous complexes. All such reaction products must then be amenable to the usual waste water treatment methods for proper disposal. Other problems are corrosion of the equipment, the necessity for maintaining the minimum effective concentration in the scrubbing fluid at all times, and considerable reagent costs. Examples of potential scrubbing reagents are KMnO_4 , NaClO , NaHSO_3 , lime water, Cl_2 , and ClO_2 ; however, no single scrubbing reagent can effectively remove all the odorous compounds from meat or poultry rendering plants.

Rationale and criteria associated with designing effective reactive scrubbing systems for controlling rendering plant odors include preconditioning of air to remove particulate matter, removal of insoluble components by condensation or adsorption, and other steps for operational improvement of odor control scrubbers. There is also a need for low- to medium-pressure drop venturi scrubbers for gross particulate matter removal. (Removal of fine particles carrying odors requires high-energy (pressure drop) scrubbers, which are usually the venturi type.) Particulate matter can also be removed by a wide variety of wet collectors and impingement devices. Demisters prevent contact tower plugging by particulate-laden gas.

For five scrubber systems evaluated, the total operating costs were approximately \$0.10/hr/1000 acfm; the air flows involved were 21,000–55,000 acfm. Approximately a 100-fold reduction in odor levels was achieved.

A Canadian rendering plant equipped with such a system was tested by EPA using modified ASTM D-1391-57 odor concentration determination methods. The scrubber inlet odor concentration ranged from 50,000–77,000 ou/scf, while the outlet concentration was 10–40 ou/scf. Sodium hypochlorite solution was used in a packed tower following a once-through venturi scrubber supplied with river water. An overall pressure drop of 10 in. of water was observed. About 10,000 cfm of the total 32,000 cfm handled was process air, largely from the blood and feather dryers; the remainder was ventilation air.

This particulate installation would be able to meet the EPA-proposed rendering plant standard of 200 ou/scf, which requires that any dilution air must be taken into account. In this case the equivalent odor concentration would be about 128 ou/scf.

The initial operation of this scrubber used potassium permanganate as the oxidizing agent in the packed tower. The subsequent substitution of the sodium hypochlorite reduced chemical costs and achieved slightly greater odor abatement. In addition, the earlier manganese dioxide residue removal problem was eliminated.

A comparison of several aqueous reagents for scrubbing indicated that, while potassium permanganate was uniformly effective in chemically oxidizing all the odoriferous substances, specific compounds were more efficiently removed by reagents depending on functional group reactions. The most effective reagents for amines, mercaptans, and aldehydes were, respectively, hydrochloric (or sulfuric) acid, sodium (or calcium) hydroxide, and sodium (or calcium) bisulfite.

In reducing the odors of aldehydes, ketones, organic acids, and organic nitrogen and sulfur compounds produced during rendering and food processing by 80–98%,

Some rendering plants adequately controlling odor

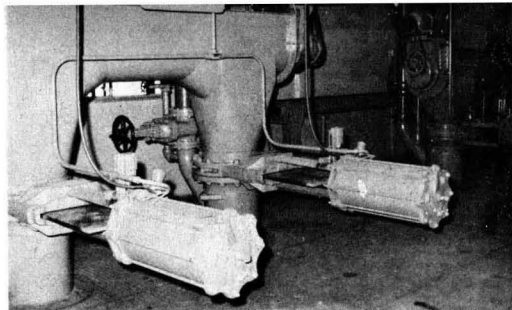
Plant	Odor control method
Baker Commodities, Inc. Los Angeles, Calif.	Incineration
Calif. Protein Products Co. Los Angeles, Calif.	Incineration
Illini Beef Co. Joslin, Ill.	Incineration and scrubber
Longueuil Meat Exporting Co., Ltd. Quebec, Canada	Scrubber
Minneapolis Hide and Tallow New Brighton, Minn.	Incineration and scrubber
Peterson Mfg. Co., Inc. Los Angeles, Calif.	Incineration
Pine State By-Products, Inc. South Portland, Me.	Scrubber
Pride Packing Co., Inc. Los Angeles, Calif.	Incineration
Reliable Grease Los Angeles, Calif.	Incineration
Stovall Tallow Co. Wylie, Tex.	Scrubber
Van Hoven Co. South St. Paul, Minn.	Scrubber
West Coast Rendering Co. Los Angeles, Calif.	Incineration

Note: The assessment of the degree of control has been made by the authors, not by EPA. The mention of company or products is not to be considered an endorsement or recommendation by EPA.

less fuel. The higher investment cost over a simple thermal incinerator is discouraging. The major deterrents, however, have been rapid catalyst poisoning with subsequent loss of activity and the inability to destroy rendering odors at temperatures lower than 1200°F. These conditions have made installations of catalytic afterburners in the Los Angeles area unsuccessful. Within a relatively short time, such installations have had to be operated like direct-fired afterburners at 1200°F or more. The Los Angeles County Air Pollution Control District states that direct-fired afterburners are ordinarily installed to incinerate smoke and organic aerosols that are difficult to burn. Emissions of this type are typical of rendering plants.

Wet scrubbing

Odor removal by gas scrubbing with water has problems as a control technique. Too many of the components already identified in rendering odors are essentially



Fresher. Modern continuous rendering plants usually emit less odor because they feature enclosed material handling

the efficiency of odor removal can be increased by raising the pH of the scrubbing solution. Here, as with all reactive odor control systems, the ultimate disposal of the reaction products and spent scrubbing solution presents a significant problem.

Waste gases from a combined slaughtering and rendering operation have been deodorized by a two-step process; the gases are first passed through a filter and sent to a tower where they are scrubbed with a weak aqueous chlorine solution. A seawater scrubber operating at 70 gpm/1000 scfm of gas gave 50–80% reduction in the odors from a fish meal dryer. Odor removal efficiency could be increased to 90% by adding 20 ± 5 ppm of chlorine to the seawater.

Ozonation

Used successfully for the treatment of sewage digestion odors in Nagoya, Japan, ozonation should be adaptable to enclosed operations for the control of noxious gases. The Japanese system, handling 56,400 acfm, required 0.37 lb of ozone per hour to maintain a 1-ppm O_3 concentration; it had (in 1968) an annual operating cost of \$290/year. With a 4-sec residence time allowed for gas mixing and reaction, ammonia concentration decreased 60%. None of the normal principal components of sewage odors (hydrogen sulfide, indole, and skatole) could be detected in the treated air effluent.

For implementation of the ozonation process, all odorous emissions from rendering process steps and the plant ventilation air should be collected by means of exhaust fans. This mixture should then be treated with a small concentration of ozone. Laboratory studies are needed to estimate the required ozone concentration and

contact time. An ozone concentration of 2–4 ppm with a minimum contact time of 4–6 sec could be used for initial studies. Ozone concentrations as high as 20 ppm may be needed even with contact times of 20–40 sec.

Adsorption and masking

Adsorption with activated carbons can be an effective and economical odor control method for emissions with low concentration of odorous compounds. The technique requires collection of both the ventilation air and the process effluent gases, and separation of particulate matter and fat droplets before adsorption to prevent plugging and inactivation of the bed. Adsorbent beds must be carefully designed and continuously monitored to avoid displacement and breakthrough of some odorants caused by the presence of more strongly adsorbed materials. Adsorption problems include batch to batch variation in adsorptive capacity, low capacity for some odorants, and, without regeneration, relatively short adsorbent life. These problems have prevented this technique from achieving popularity with renderers.

Although activated carbons are the most common adsorbents in use for odor control, their application is limited to the control of low-temperature gases of low-odor concentration. Rendering plant emissions should be cooled to 120°F or less before adsorption can be used for effective odor control.

Activated carbon could be used to control odor emissions from rendering plant operations. The control system, consisting of a combination condenser-deodorizer, reduces blowovers from the cooker. The abatement cost (in 1962) was \$550/year. Activated carbon was chosen because of its low cost, high capacity for organic compounds, and simplicity of operation.

Masking and counteraction techniques have not proved suitable for rendering operations. Not only are too many different chemical species present, but the added chemicals merely compound the problem by becoming air pollutants themselves. The great disadvantage of these procedures is that the odorous compounds are not removed from the rendering plant effluent air.

R&D needs

Air pollution control regulations in some states call for either incineration of the cooker and expeller off-gases at 1400–1600°F for not less than 0.3 sec or other treatment to give equivalent results. Thus, there is a great need for the development of low-cost catalytic afterburners, which are not affected by catalyst poisons, to meet the odor control regulations both effectively and economically.



Robert M. Bethea is on the faculty of Texas Tech University where his primary research interests are in design of control systems for agricultural particulate matter, in situ analysis of reactive gases, and controlling odors from agricultural operations.



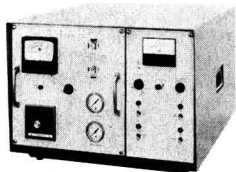
Belur N. Murthy is a research chemical engineer with Control Systems Laboratory, National Environmental Research Center. His interests have evolved from odors and hydrocarbons to the general area of control of pollutants from stationary sources. Address inquiries to Dr. Murthy.



Donald F. Carey is a chemical engineer recently transferred to EPA's Stationary Source Enforcement Division, Technical Support Branch. Formerly his responsibilities included developing new stationary source performance standards for sulfuric acid and rendering plants.

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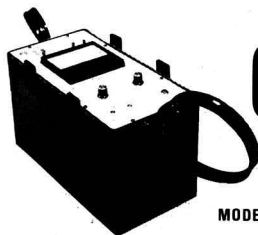


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Another approach to the solution of rendering odor problems is the development and demonstration of regenerable package sorption systems. The advantages of such systems are simplicity of operation, applicability to a wide variety of installations, and economic acceptability to small processors. Engineering and economic feasibility of using the combined adsorption/regeneration-incineration system for rendering plant odor control require detailed investigation. Of particular importance for the successful implementation of sorption systems is the removal of fatty particulate matter from the air and process streams prior to the package adsorption unit. This procedure is necessary to avoid plugging of the bed, thereby lengthening the time between required bed regenerations.

A coordinated research effort is also needed to find a scrubbing chemical or mixture which can be used for the wide variety of odorous compounds present. Sodium bisulfite or calcium perchlorate can be used to control the odors associated with aldehydes; lime water can be used to remove ammonia and mercaptans; hydrogen sulfide can be removed by potassium permanganate or sodium hypochlorite which are effective oxidants for many other organics. This research should center on finding a scrubbing mixture which is highly effective, inexpensive, regenerable or recyclable, and amenable to standard waste water treatment operations. Concentration(s), pH value, residence time, mass transfer area, and contacting method (packed, spray, or tray tower) should be investigated. A preliminary study of these factors has been included in a research effort, supported by EPA and the Fats and Proteins Research Foundation, which is currently under way at the Research Institute of the Illinois Institute of Technology. The goal of this research is to develop an effective and economical method for rendering plant odor control.

Other possible research areas with potential for achieving economical control of odors from rendering operations are:

- investigation and development of economical, poison-resistant catalysts for application in more attractive catalytic incineration processes
- development of analytical techniques and instrumentation for identification and quantitative evaluation of the level of odorous pollutants in process streams and in effluent streams
- investigation of refrigeration or freezing as a means of minimizing decomposition and odor formation in materials prior to rendering
- study of solvent extraction of fats or other low-temperature processes as possible alternates to high-temperature cooking operations
- better housekeeping in plant operations.

Additional reading

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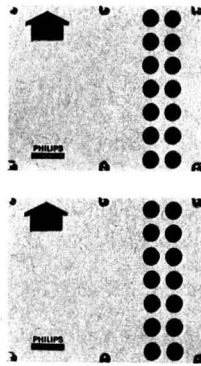
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FEATURE

Conserving energy with heat storage wells

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University of California, Berkeley, Calif. 94705

Electric and gas utilities have embarked upon major campaigns to promote conservation of energy because of public pressure and the short supply of clean fuels. Construction of new central-station electric plants has encountered such severe resistance that the prospect of brownouts is very real. Much of this resistance relates to the thermal pollution which results from the need to dispose of roughly two units of low-quality (that is, low-temperature) heat energy for each unit of electrical energy that is generated.

Recent studies at General Electric's Center for Advanced Studies (TEMPO) show that thermal pollution could be greatly reduced and substantial energy conservation could result from large-scale application of a total-energy approach under which utilities would produce and market both electricity and useful heat.

Total-energy systems of relatively small capacity are well known. They are becoming popular for industries, apartment buildings, and large commercial complexes. Internal combustion engines, steam turbines, and gas turbines (more precisely, combustion turbines) are used to drive electrical generators. Exhaust heat, supplemented as necessary from auxiliary boilers, supplies steam or hot water for nearby space heating, cooling (via an absorption cycle), hot water, and process heat requirements. A number of electric utilities are also in the district heating business. Consolidated Edison in New York City serves the largest such load.

This article covers the key question that arises in considering large-scale application of the total-energy approach: Is it feasible to store large amounts of high-quality by-product heat for several months, in order to match the production of the heat to seasonal demand for it? The answer to this question, employing a novel approach, appears to be affirmative.

Storage of relatively small amounts of heat has been accomplished by using hot water tanks, rocks or masonry, and materials that melt or vaporize. However, known methods are too expensive to be attractive for a large total-energy system.

The preliminary analysis described here indicates that large quantities of useful heat may be stored underground in special water wells, with more than three-fourths of the heat being recoverable after 90 days. The economics appear quite favorable.

Hydrology and heat loss of a heat-storage well

For purposes of a preliminary analysis of the feasibility of storing heat underground, a 40,000 gph well was theoretically considered. Equivalent to about 1 mgd, this moderately large well is assumed to be roughly 500 ft deep, with the lower 100 ft penetrating a confined aquifer (Figure 1).

The hydrology and the heat losses were examined for a 90-day cycle of hot water injection followed by withdrawal until the temperature of the withdrawn water was at an arbitrary lower limit. A 90-day period bridges the spring and the fall seasons, when space heating and air-conditioning loads may be too light to utilize all of the by-product heat from electric power generation.

Injected hot water will have markedly different physical properties from those of natural groundwater. Not only will the hot water be as much as 10% less dense than the cold groundwater, but its viscosity will be about one sixth that of the cold water being displaced. The viscosity ratio of two fluids in a porous medium directly affects the relative permeability of each, an effect referred to as the mobility ratio. The density and viscosity differences will cause the hot water to tend to override the cold water and to displace it from the top of the aquifer downward in a wedge shape (Figure 1).

Hydrological assumptions include: The aquifer is confined, homogeneous, and has a porosity of 25%; there is no mixing at the hot-cold interface; and the artesian head is sufficient to maintain water at 340°F in a liquid state, when water at this temperature is injected or withdrawn. Lateral displacement of the hot water due to natural flow of the groundwater was neglected.

Geohydrological assumptions upon which heat loss calculations are based are: The aquifer is 100 ft thick; it is confined on top by a layer of clay; the unconfined aquifer above the clay is initially, and remains at, a temperature of 60°F; the initial temperature of the confined aquifer is 60°F, and its specific heat is 0.2 Btu/lb-°F.

An injection well at a steady flow of 1 mgd will receive in 90 days a total volume of 12.1 million ft³ of water, which will spread out into an inverted cone. For the stated assumptions, the top surface of the cone will form a circle with a radius of 600-700 ft. To store the equivalent volume of hot water above ground would require a tank of approximately 200 ft in radius and 100 ft high, plus insulation. This comparison gives a clue to the attractiveness of storing heat in aquifers. A number of such tanks would be required, which would be aesthetically objectionable if above ground and too expensive to be feasible whether above or below ground. Wells, however, are unobtrusive and require very little land, but they can tap large volumes of underground storage space.

The required aquifers can be found in many—not all—of the locations where the use of aquifers for heat storage might be considered. Hot wells appear to be quite acceptable environmentally if elementary precautions are taken to avoid locating them too close to producing water wells.

A complete heat transfer solution would require a three-dimensional transient calculation, which was not

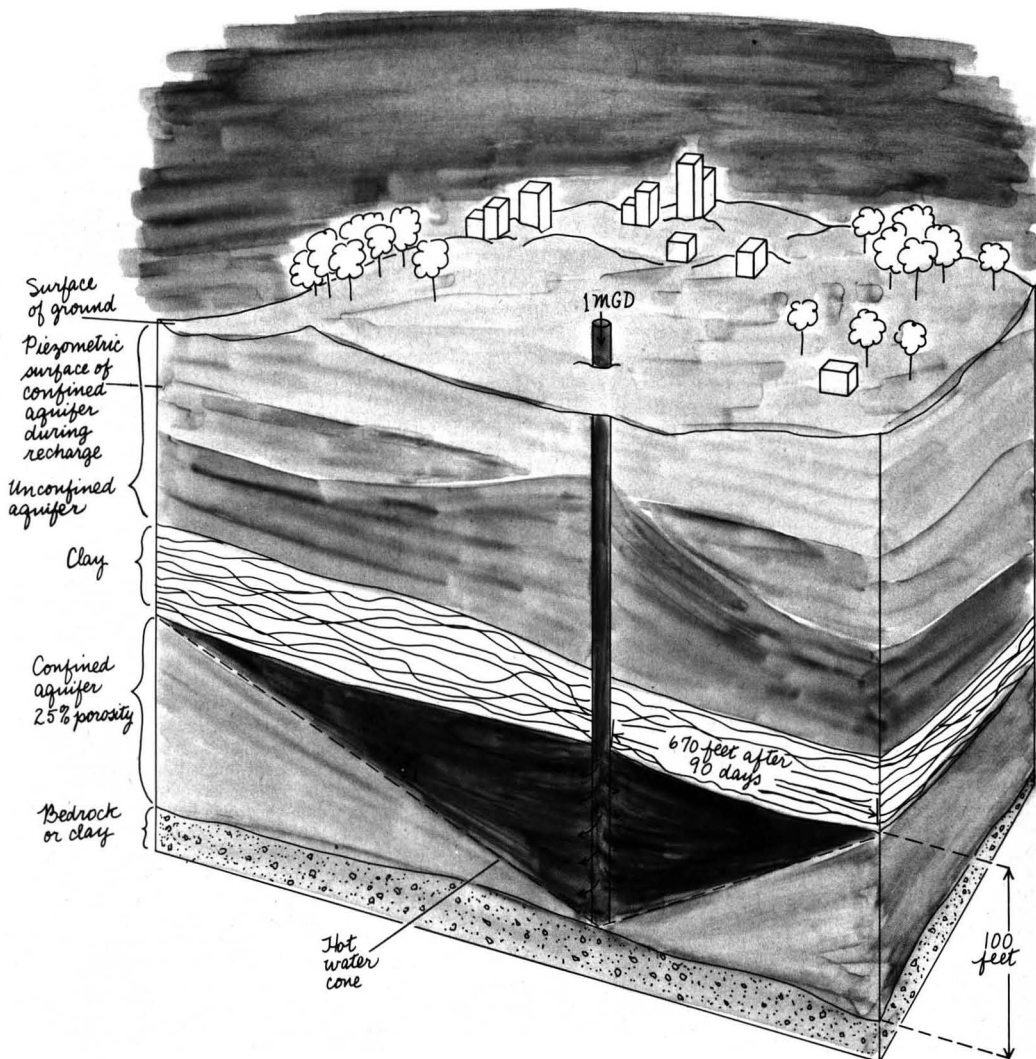


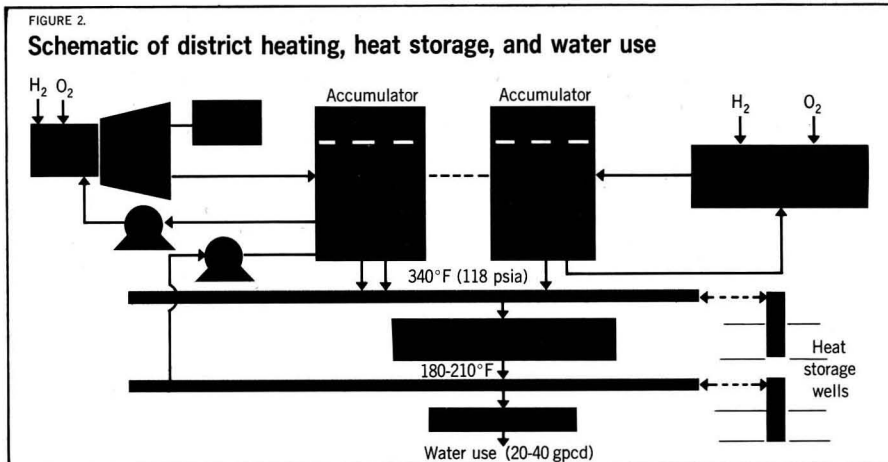
FIGURE 1.
In a theoretical 500-ft heat storage well, the injected hot water will spread out into an inverted cone with a radius of approximately 700 ft. In spite of heat loss to the confined and unconfined aquifers, 75% of the heat can be recovered and marketed by electric and gas utilities

attempted. Approximations were made to reduce the calculation to one dimension and to simplify the form of the transient behavior.

Hot water is assumed to be injected in "slugs" of 320,000 gal each (8 hr of flow) rather than continuously, and temperature equilibrium is assumed to be reached very rapidly compared with the time required for significant heat conduction. Heat is lost by conduction through the top confining layer to the constant-temperature unconfined aquifer and by warming the confined aquifer material to the temperature of the water in which it is immersed. As each successive slug is injected, the radius of the hot-water cone steps outward. Similarly, when water is withdrawn, the temperatures are calculated stepwise as the cone shrinks. The limit of withdrawal is set by the minimum hot water temperature considered usable.

Two cases were calculated. Case 1 assumed injection for 90 days of superheated water at 340°F, followed by withdrawal at 40,000 gph until the temperature dropped to 300°F. In Case 2 the injection temperature was 210°F and the minimum withdrawal temperature was 180°F.

As hot water is injected for the first 90-day cycle, the aquifer material must be warmed from the assumed am-



bient of 60°F. However, during the second injection cycle, the aquifer temperature is already above the original ambient temperature, and a larger fraction of the injected hot water can be withdrawn before encountering minimum temperature water. Five injection-withdrawal cycles brought the aquifer essentially to equilibrium conditions. The computed fractions of heat and water that can be recovered are shown in Table 1. Showing heat recovery efficiencies of up to 86%, the promise of water wells as a heat storage medium is clear.

Markets for heat

Some perspective in evaluating the potential demand for district heat is provided by an estimate that the residential electrical load in 1970 was about evenly divided between two categories. One can be accommodated by heat: water heating, space heating, and absorption-cycle air conditioning. The other requires electricity: lighting, cooking, and appliances such as TV sets and refrigerators. Each of the two categories consumed about 2.2 quadrillion Btu.

Water heating accounts for a surprisingly large fraction of the total energy consumption of the U.S.—roughly 4%—which is equal to almost one half of the total energy that is consumed as electricity. Water at a temperature of 180°F or higher can satisfy the requirement for hot water.

Space heating is estimated to be 20% of the total energy consumption of the U.S. This heat energy is roughly equivalent to the total amount of energy used in generating electricity or about three times the energy consumed as electricity. In most parts of the U.S., space heating is needed during less than half of the year.

Air conditioning accounted for only 2.5% of total energy consumed nationally in 1968, but the demand is growing at over 10% per year and accounts for much of the need for additional electrical generating capacity. Summer peak loads on electric utilities became essentially equal to December peaks in the late 1950's, and by 1970 exceeded December peaks by 10%.

Steam or water temperatures of 300°F or higher are desirable for space heating and air conditioning, although 180°F water can be used. Industrial process heat accounts for about 10% of total U.S. energy consumption. About half of this demand can be met by steam at pressures of 100 psi or lower.

From these facts, one concludes that there is a potential market for all of the high-quality heat that can be produced as a by-product of electrical power generation, but that some of the by-product heat would require seasonal storage. A second conclusion is that the total-energy ap-

proach including heat storage would allow substitution of heat for electricity and fuels. A consequence could be a significant reduction in the rate of increase in demand for electricity and fuels.

Total-energy system considerations

Electrical demands must be met precisely and instantaneously as switches are turned on and off. The district heating load will not coincide timewise with the electrical load. Neither will the magnitudes of the two types of loads match the exhaust heat and shaft horsepower output of the combustion turbines or other prime movers. Supplementary heat can be provided by auxiliary boilers when the heat load exceeds the exhaust heat available. Conversely, heat must be stored when electrical demand causes more exhaust heat to be available than is needed at the moment. The load-matching problem and the requirements for heat storage depend principally upon the large seasonal fluctuations in demand for space heating and air conditioning. Water heating and process heat loads may be expected to be less seasonal.

A second important system consideration is that heat, unlike fuels and electricity, cannot be transmitted more than a few miles without substantial losses. For the total-energy utility concept to be applicable, electrical generating stations (and heat-storage wells) will have to be located close to heat loads. This requirement is contrary to the general trend in siting central stations which have tended to become larger, for economies of scale and other reasons, and to be sited at increasing distances from the electrical loads they serve. In recent years, many of the reasons for remote siting are environmental: to meet nuclear safety standards, to obtain adequate cooling water, to meet air quality standards. Another en-

TABLE 1
Heat and water recovery
(From 1 mgd hot well after 90 days)

Injection temp., °F	Temp. of withdrawal, °F	Cycle	Fraction recovered	
			Heat	Water
340 (Case 1)	300	1	0.72	0.81
		2	0.77	0.87
		5	0.79	0.88
210 (Case 2)	180	5	0.86	0.94

vironmental reason now being advanced for locating large generating stations at a considerable distance from the load area is to reduce the heat-island effect of cities.

That environmental considerations cannot be fully satisfied simply by building large plants at greater distances from load centers is evident from the difficulties that electric utilities are encountering in obtaining site and construction approval for new plants. Another increasingly important difficulty is the opposition on aesthetic grounds to construction of overhead transmission lines, particularly within cities.

Energy can be transmitted in the form of fuel, through pipelines, more cheaply than as electricity in overhead lines. The implications of this fact were explored at TEMPO. A number of alternative systems were synthesized and evaluated. As one of the alternatives, small generating stations would be located at substation sites. Clean fuel would be supplied via pipelines to combustion turbines, and electricity would be distributed via buried cables. Such a system appears to be quite acceptable, environmentally and economically. The concept is consistent with recent sharply upward trends in use of combustion turbines by electric utilities. Further exploration of the feasibility of a total-energy utility system, using the dispersed-turbine approach, appears to be amply justified.

Combustion turbines began in the early 1960's to be installed by electric utilities to handle peak loads. Combustion turbines cost much less than steam plants per kilowatt of capacity, but, in general, are less efficient. These factors favor peaking duty rather than base loading. Now, however, advanced combustion turbines appear destined for use as mid-range and even base-load prime movers, for several reasons. Their efficiency and reliability are becoming competitive with steam turbines. They can meet environmental requirements much more readily than can steam plants, because of their comparatively small size, flexibility of siting, and ability to operate without cooling water or towers. Boilers now require essentially the same clean fuels that are burned by combustion turbines. Turbines can be procured and installed in significantly shorter time than steam plants and have less impact on utility debt structures—some turbines are leased.

Combustion turbines now operate at thermal efficiencies of 25–35%. Their exhaust temperature is about 1000°F, which is also a typical throttle temperature for modern steam turbines. Rather than allowing exhaust heat to be wasted, combined-cycle plants employ heat exchangers (for example, boilers) to recover the exhaust heat, generate steam, and drive steam turbines. Overall efficiency is substantially improved, but the steam turbine system requires condensers and cooling water or towers. These can impose severe environmental problems. If the steam were used instead to supply heat loads, the environmental problems could be avoided.

Heat distribution

The more dense the electrical and heat loads, the more efficient will be the distribution of heat. The optimal size, number, and location of combustion turbines will be determined by the density and nature of the two loads to be served.

One heat distribution system that has been visualized includes two manifolds connecting heat sources and heat loads. One manifold would collect hot water or steam at about 340°F from the heat exchangers in the combustion-turbine exhausts and deliver it to the heat loads. The second manifold would return water at about 180°F to be reheated in the heat exchangers. A continuous circulation of water would be maintained in each manifold to minimize temperature variations with changes in the amounts of heat produced and consumed.

Space heating, air conditioning, process heat, and water heating loads would be served by heat exchangers on the customers' premises, fed from the 340° manifold and returning water to the 180° manifold. Heat would be supplemented by auxiliary boilers or stored in wells as necessary to balance the heat produced and the heat demanded.

A heat exchanger in the 1000° exhaust stream of a combustion turbine, with a water inlet temperature of 180°, could recover energy roughly equivalent to the shaft output of the turbine. To illustrate the approximate amounts of electricity, heat, and water involved, suppose that turbines driving 100,000 kW of electrical generating capacity are interconnected via the heat distribution manifolds. This electrical capacity might serve the average needs of 50,000 to 60,000 people, using a rough approximation based on total national generating capacity and population.

Assuming a 50% load factor, 1,200,000 kW-hr of electricity and the same amount of heat would be produced per day. To absorb this amount of heat, 3 mgd of water would be required, at a temperature rise of 160°F (340–180°). In the climate of Philadelphia, Pa., the residential needs for space heating, air conditioning, and water heating of about 20,000 people could be served, allowing 30% loss in the heat distribution and storage system.

An advanced system

A more advanced system would employ hydrogen-oxygen turbines. That a "hydrogen economy" will evolve within the next one or two decades, due to the shortage of fossil fuels and other considerations, has been postulated by a number of investigators. Hydrogen and oxygen would be manufactured by splitting water.

The exhaust from a hydrogen-oxygen turbine would be pure steam. The turbine can be designed to exhaust at whatever temperature is dictated by heat-energy requirements, with corresponding backpressure on the turbine (at 340°F, 118 psi). Thus, a backpressure hydrogen-oxygen turbine could produce steam to be fed directly into a steam accumulator and then into the 340° manifold of a heat distribution system as shown in Figure 2. Since full thermodynamic credit can be taken for the heat in the exhaust, the effective efficiency of the hydrogen-oxygen turbine is very high in spite of the backpressure. Losses due to friction, auxiliary pumps, and leakage should amount to 10% or less. For energy conservation this approach is extremely attractive.

An intriguing feature of the hydrogen-oxygen turbine approach is that potable water will be recovered as the hydrogen and oxygen burn. In the illustration above, with turbines generating 1,200,000 kW-hr per day of electricity, about 140,000 gpd of pure water would be produced by the turbines and added to the 3 mgd of cooling water. Thus, water would become another salable by-product. The 140,000 gpd of water would satisfy the hot water needs of 3500–7000 people, at 20–40 gal per capita day. Water for this purpose could be withdrawn directly from the 180° manifold, piped into home hot water tanks, used, and wasted in the usual manner into sanitary sewers.

If the heat load were zero, three 1-mgd wells would be required to store the 3 mgd of hot water from 100,000 kW of turbine capacity. Conceivably, another three 1-mgd wells would be required as sources of cool water, if none was available from other suitable sources. A reasonable assumption for estimating costs is that a total of four 1-mgd wells would suffice. The total cost of four 1-mgd wells, cased and equipped with pumps, would be \$200,000–300,000 plus a modest land cost. By way of comparison, a cooling tower at \$20–40 per kW, for the steam portion of a combined-cycle plant, would cost \$1,000,000–2,000,000 plus a substantial cost for land.



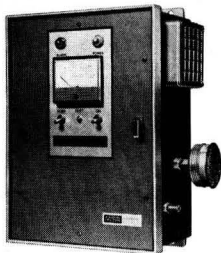
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To design and operate optimal systems that supply electricity, heat, and perhaps water is a major new problem to be faced by a utility contemplating the total-energy approach. Probably the institutional problem of discovering appropriate organizational, franchising, financial, and public-acceptance mechanisms is at least as formidable as the technical problem. However:

- hot water can in theory be stored in special water wells, and as much as 86% of the heat can be recovered after 90 days

- heat-storage wells may be the key to utilizing high-quality heat produced as electricity is generated; the seasonal heat loads can, through heat storage, be matched to electrical demand. Total-energy utilities become feasible

- environmental considerations suggest that small generators located at substation sites may supplant construction of large distant stations and transmission lines. These small generators would be ideally suited to a total-energy utility

- energy can be conserved and thermal pollution greatly reduced by adopting a total-energy approach, with heat storage.

Additional reading

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Charles F. Meyer is project manager, TEMPO, General Electric Co. Center for Advanced Studies. He manages projects involving research in water resources, electric utility systems, and environmental quality. Currently, Mr. Meyer is responsible for a two-year project to develop concepts and methodology for monitoring the quality of U.S. groundwater. Address inquiries to Mr. Meyer.



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- Burnet, F. M., Stanley, W. M., Eds., "The Viruses," Vol. 1, pp 609-15, Academic Press, New York, N.Y., 1959.
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Measurement of Ultraviolet Radiation Intensity in Photochemical Smog Studies

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■ The most widely used technique of measuring ultraviolet radiation intensity in photochemical smog studies is to irradiate NO₂ in a nitrogen atmosphere. In the past a fictitious first-order rate constant, k_d , has been used to characterize the nonlinear NO₂-time behavior in such a system. The inadequacy in the use of k_d stems from the need to extrapolate the NO₂-time curve to zero time. The actual photolysis rate constant for NO₂ dissociation, k_1 , provides an unambiguous measure of uv intensity. If the NO₂ photolysis is performed in the usual fashion, we show that k_1 can be computed *directly* from the NO₂-time data by the equation,

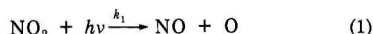
$$k_1 = \frac{1}{2\Delta t} \left\{ (1 + R_1 - R_2) \ln \frac{[\text{NO}_2]_0}{[\text{NO}_2]} + R_2 \left[\frac{[\text{NO}_2]_0}{[\text{NO}_2]} - 1 \right] \right\}$$

where the constants R_i are defined in the text. The validity of this equation has been established both experimentally and by computer simulation.

It is now widely accepted that among the variable factors in smog chamber experiments, such as temperature, surface-to-volume ratio, and relative humidity, the intensity of ultraviolet radiation is one of the most critical parameters. The radiation intensity strongly governs the time scale upon which the various processes, such as the rate of conversion of NO to NO₂, occur. Recently there has been considerable interest in the development of kinetic mechanisms for photochemical smog (Hecht and Seinfeld, 1972; Niki et al., 1972; Hecht, 1972). Knowledge of the ultraviolet radiation intensity is vital to the success of computer simulations of smog chemistry, since the correctness of the rate constant for the primary process, the photolysis of NO₂, determines the validity of the results for nearly all of the subsequent steps.

Physical measurement of uv intensity by various spectroradiometric techniques would, of course, be desirable from the standpoint of comparing the sources of artificial sunlight used in various smog chambers with one another and with the ultraviolet portion of the solar spectrum. However, such absolute measurements require specialized apparatus which is complex and relatively expensive. Since it was first suggested by Tuesday (1961), the photolysis of NO₂ in nitrogen has become more or less universally accepted as the way of calibrating uv sources used in photochemical smog studies. The rationale for this meth-

od is that the fundamental photochemical process in smog formation is the photolysis of NO₂:



and that the rate of this reaction determines, to a large extent, the rate of the overall process. Thus, it is not necessary to measure the spectral distribution of the radiation, only the first-order decay constant k_1 .

The assumption implicit in smog chamber experiments is that artificial radiation which drives Reaction 1 at a rate comparable to that observed with natural sunlight will also allow the experimenter to simulate all of the other processes which occur in the atmosphere. This assumption is not completely valid, since other species present in smog can also undergo photolysis or photoexcitation and the rates of these processes, in general, have a wavelength dependence different from that of NO₂. To a good approximation, however, these other processes can be neglected and the rate of the primary process can serve as a useful measure of uv intensity.

The key problem in using a system of NO₂ photolysis in N₂ is to determine the photolysis rate constant k_1 from the NO₂ concentration vs. time data. It is well known that the photolysis of NO₂ in N₂ is not a first-order process because of a number of side reactions that take place in addition to Reaction 1. Thus, the ln NO₂ concentration vs. time data will not lie on a straight line. In spite of this fact, it has been common practice to define a fictitious first-order rate constant k_d for NO₂ disappearance in N₂. The fictitious rate constant k_d is defined by

$$k_d = \lim_{t \rightarrow 0} \frac{-d \ln [\text{NO}_2]}{dt} \quad (2)$$

that is, the slope of the NO₂ decay curve extrapolated to time zero. Since k_1 , the desired parameter, has been considered a difficult quantity to measure directly, it has become common practice to use k_d rather than k_1 as the measure of light intensity in smog chambers. The accuracy of using this approach to calculate k_d is governed by how rapidly and accurately the NO₂ concentration can be determined after the lights are turned on, time being particularly important when the light intensity is strong.

The primary object of this work is to eliminate entirely the quantity k_d in favor of direct measurement and reporting of k_1 , the primary photolysis rate constant. As a result of both experimental and theoretical studies, we

¹ To whom correspondence should be sent.

have developed a simple method of determining directly the actual rate constant for NO₂ photolysis, k_1 , in systems of NO₂-N₂.

Mechanism of NO₂ Photolysis in N₂ and O₂

The mechanism generally employed in interpreting the photolysis of ppm levels of NO₂ in N₂ and O₂ is presented in Table I. The first 10 reactions were proposed by Ford and Endow (1957) for the system free of O₂—Reaction 11 has been added for the case in which O₂ is present. The primary process, Reaction 1, is dependent on light intensity; all other reactions result from the highly reactive nature of the oxygen atoms formed in Reaction 1.

Ford and Endow (1957) and Schuck et al. (1966, 1969) investigated the mechanism for NO₂ photolysis. When there is no O₂ present initially, it is possible to assume that O, O₃, NO₃, and N₂O₅ are in pseudosteady state. Also under these conditions Reactions 8 and 11 can be neglected. Using these assumptions, Schuck et al. (1966, 1969) derived the following equation for the rate of change of NO₂ concentration:

$$\frac{-2k_1}{d \ln[\text{NO}_2]} = 1 + \frac{k_2[M]}{k_4} + \frac{k_7[M][\text{NO}]}{k_4[\text{NO}_2]} + \frac{k_2[M][\text{O}_2]}{k_4[\text{NO}_2]} \quad (3)$$

where the k 's are the rate constants for the corresponding reactions in Table I.

If k_d is defined by Equation 2, then Equation 3 can be written

$$\frac{2k_1}{k_d} = 1 + \frac{k_2[M]}{k_4} + \frac{k_7[M][\text{NO}]}{k_4[\text{NO}_2]} + \frac{k_2[M][\text{O}_2]}{k_4[\text{NO}_2]} \quad (4)$$

Equation 4 seems complex but it can be readily interpreted. In the absence of any reactions except 1 and 4, all oxygen atoms formed would react with NO₂ to form NO and O₂. This gives an overall quantum yield of 2—two molecules of NO₂ disappear for each photon absorbed. This would give the relationship $k_d = 2k_1$ and would hold if the experiment were run without N₂ at low pressure ($M = 0$). In the actual case, however, various species compete with NO₂ for the O atoms. The effect of this competition is expressed in the last three terms in Equation 4. These are the ratios of oxygen-atom reaction rates by other pathways to the rate of Reaction 4.

Schuck et al. (1966) analyzed their experimental data using Equation 4 and obtained values of the various rate constants which they compared to previous determinations, some of which have large uncertainties. These are in good agreement with previous evaluations except for k_4 , for which they derive a value 50% higher than the number generally accepted (Baulch et al., 1970).

What was apparently not recognized previously is that Equation 3 may be integrated analytically under the assumption that NO and NO₂ contain almost all of the NO_x at any instant, i.e., that

$$[\text{NO}] = [\text{NO}]_0 + [\text{NO}_2]_0 - [\text{NO}_2] \quad (5)$$

The result of the integration of Equation 3 subject to Equation 4 is the following fundamental expression:

$$k_1 = \frac{1}{2\Delta t} \left\{ (1 + R_1 - R_2) \ln \frac{[\text{NO}_2]_0}{[\text{NO}_2]} + R_2 \left[\frac{[\text{NO}_2]_0}{[\text{NO}_2]} - 1 \right] + (R_2[\text{NO}]_0 + R_3[\text{O}_2]) \left[\frac{[\text{NO}_2]_0 - [\text{NO}_2]}{[\text{NO}_2]_0[\text{NO}_2]} \right] \right\} \quad (6)$$

where $\Delta t = t(\text{final}) - t(\text{initial})$ and $R_1 = k_5[M]/k_4$, $R_2 = k_7[M]/k_4$, and $R_3 = k_2[M]/k_4$.

Equation 6 may be simplified if the initial concentrations of NO and O₂ are zero,

$$k_1 = \frac{1}{2\Delta t} \left\{ (1 + R_1 - R_2) \ln \frac{[\text{NO}_2]_0}{[\text{NO}_2]} + R_2 \left[\frac{[\text{NO}_2]_0}{[\text{NO}_2]} - 1 \right] \right\} \quad (7)$$

In the remainder of this paper, we establish experimentally the validity of the mechanism in Table I (the Ford-Endow mechanism) for the photolysis of NO₂ in N₂ and verify the assumptions made in the derivation of Equation 7.

Photolysis of NO₂ in N₂

Experimental System. A long-path infrared system similar to that described by Pitts (1969) was employed. A 90-liter borosilicate glass reactor encloses the sample cell and optics. The reactor is surrounded by twenty 20-W fluorescent tubes. In the initial experiments, 10 black lights and 10 sun lamps were used. However, the sun lamps make a relatively small contribution to the rate of NO₂ photolysis because the absorption coefficient is lower for sun lamps than for black lights and because shorter wavelength uv is more strongly absorbed by the reactor walls.

Thus, in later experiments, 20 black lights were employed to provide a rate of photolysis more nearly comparable to that produced by intense sunlight.

The system is evacuable to 10⁻⁶ torr. The interior metal surfaces, except the mirrors, have been coated with a nonporous fluorocarbon resin. The spectrophotometer is a Perkin-Elmer Model 521 equipped with scale expansion which, in effect, allows the maximum optical path length of the cell to be increased electronically from 40–800 meters. Temperature within the reaction cell is monitored continuously. External forced-air cooling maintains the cell within 2°C of ambient temperature during irradiation.

Trace gases are introduced into the LPIR cell at known pressures (measured with a silicone oil manometer) from calibrated volumes. The final pressure is brought to 1 atm with Ultra Pure (Airco 99.998%) grade nitrogen. The NO₂ was purified by pressurizing with O₂ followed by vacuum distillation.

Experimental Results. In the LPIR, we obtain a continuous record of NO₂ concentration as a function of time.

Table I. Reactions and Rate Constants for Photolysis of Nitrogen Dioxide in Nitrogen and Oxygen

No.	Reaction	Rate constant	Reference
1.	NO ₂ + $h\nu$ → NO + O	To be estimated	
2.	O + O ₂ + M → O ₃ + M	2.33×10^{-5} ppm ⁻² min ⁻¹	Johnston (1968)
3.	O ₃ + NO → NO ₂ + O ₂	2.95×10^1 ppm ⁻¹ min ⁻¹	Johnston and Crosby (1954)
4.	O + NO ₂ → NO + O ₂	1.38×10^4 ppm ⁻¹ min ⁻¹	Schuck et al. (1966)
5.	O + NO ₂ + M → NO ₃ + M	4.50×10^{-3} ppm ⁻² min ⁻¹	Schuck et al. (1966)
6.	NO ₃ + NO → 2 NO ₂	1.48×10^4 ppm ⁻¹ min ⁻¹	Schott and Davidson (1958)
7.	O + NO + M → NO ₂ + M	2.34×10^{-3} ppm ⁻² min ⁻¹	Kaufman (1958)
8.	2 NO + O ₂ → 2 NO ₂	7.62×10^{-10} ppm ⁻² min ⁻¹	Glasson and Tuesday (1963)
9.	NO ₃ + NO ₂ → N ₂ O ₅	4.43×10^3 ppm ⁻¹ min ⁻¹	Schott and Davidson (1958)
10.	N ₂ O ₅ → NO ₃ + NO ₂	1.38×10^1 min ⁻¹	Mills and Johnston (1951)
11.	NO ₂ + O ₃ → NO ₃ + O ₂	1.06×10^{-1} ppm ⁻¹ min ⁻¹	Johnston and Yost (1949)

Any departure from linearity of the plot of $\ln [\text{NO}_2]$ vs. time is immediately apparent from the experimental data. Figure 1 shows the results of such an experiment under conditions at which one typically measures k_d . The departure from linearity is appreciable even for short irradiation times. The effect is even more pronounced at high light intensity, such as is present in most environmental chambers.

In our case, the problem of nonlinearity is easily overcome by extrapolating back to $t = 0$ and taking the initial slope of the curve as the value of k_d . For experimental situations where the NO_2 concentration cannot be monitored continuously as a function of time, this extrapolation could not be performed.

Two series of experiments were performed to investigate the validity of Equation 4. This equation may be simplified under certain experimental conditions. If the O_2 concentration is below 50 ppm, the last term is small and may be ignored. Further, at the beginning of photolysis, no NO is present so the second to last term is also negligible since the NO_2 decay rate is extrapolated to zero time.

The first series of experiments involved varying the pressure of M in the k_d determination. Equation 4 predicts that at zero pressure of added N_2 , $k_1 = k_d/2$. Therefore, this approach should give the best value of the absolute light intensity in terms of k_1 . Figure 2 shows the results of these experiments which were run with varying amounts of added N_2 , corresponding to 0, 0.1, 0.4, 0.7, and 1.0 atm N_2 . If one neglects the datum for no added N_2 , the least-squares line of the remaining points extrapolates to $k_1 = 0.144 \text{ min}^{-1}$ at $P_{\text{N}_2} = 0$. From the slope of the line a value of $k_5/k_4 = 0.27 \times 10^{-6}$ can be calculated directly. The experimental point at $[\text{M}] = 0$ ($k_d^{-1} = 5.0 \text{ min}$) is probably not valid, since at this pressure (5 mtorr) diffusion to the walls is rapid: those reactions which require a third body at higher pressures would be expected to occur, instead, on the walls. At pressures above 0.1 atm, wall effects are negligible. In these experiments, it was necessary to correct for deviation from the Beer-Lambert law since the ir absorption of NO_2 is strongly pressure dependent.

In another series of experiments, varying amounts of NO were added to the NO_2 before photolysis. Assuming the last term in Equation 4 is small, it may be rearranged to the form

$$\frac{1}{k_d} = \frac{1 + R_1}{2k_1} + \frac{R_2[\text{NO}]}{2k_1[\text{NO}_2]} \quad (8)$$

Thus, a plot of k_d^{-1} vs. $[\text{NO}]/[\text{NO}_2]$ for these experiments would be expected to be linear. This is shown in Figure 3. The linearity is excellent and the following relationships can be derived:

$$R_2 = 2k_1 \times \text{slope} \quad (9)$$

$$\text{intercept} = \frac{1 + R_1}{2k_1} \quad (10)$$

Since k_1 is known from the first series of experiments, a value of R_2 can be calculated from Equation 9. The result is $R_2 = 0.16$. Equation 10 may be used to check on the internal consistency of the data with the mechanism. From the values of k_1 and R_1 found in the first series of experiments, a value for the intercept in Figure 3 may be predicted. The predicted value is 4.41 min, while the actual intercept is 4.28 min.

Validation of the Ford-Endow Mechanism and Estimation of k_1 . A computer simulation of the Ford-Endow mechanism for the photolysis of NO_2 yields results which are in excellent agreement with the experimental results over a wide range of initial conditions. A comparison for

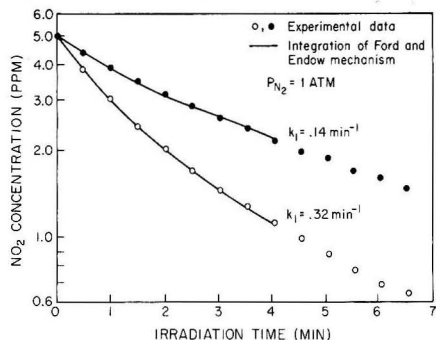


Figure 1. Photolysis of NO_2 in N_2 at two different light intensities

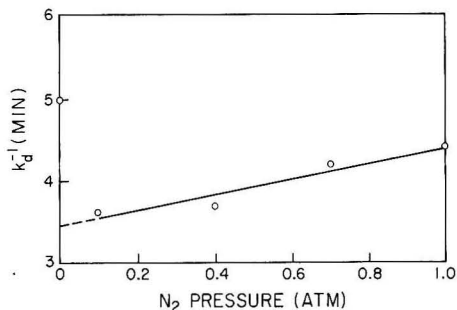


Figure 2. Pressure dependence of k_d determination (photolysis of 5 ppm NO_2 at varying pressure of N_2)

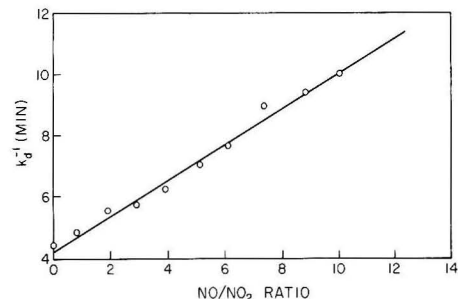


Figure 3. Variation of k_d with added NO (photolysis of mixtures of 5.0 ppm NO_2 and varying NO)

two typical runs is shown in Figure 1. The curves are from the simulation and the points indicate experimental data. Optimum agreement was obtained using the rate constants of Schuck and Stephens (1969), including the larger value of k_4 discussed above. The curves in Figure 1 can also be generated from the integrated form of the rate expression, Equation 7. The latter are identical to the computer simulation.

The simulation also computed the concentrations of all nitrogen-containing species appearing in the mechanism. The results indicate that the assumptions made in deriving and integrating Equation 3 are indeed valid.

Table II shows the results of the estimation of k_1 by Equation 7 for two types of systems: varying initial NO_2 concentrations with zero initial NO concentration, using

Table II. Summary of NO₂ Photolysis Data and Estimates of k₁

[NO ₂] ₀ (ppm)	[NO] ₀ (ppm)	k ₁ (min ⁻¹)	No. of lamps
1.00	0.0	0.319	20 BL
3.11	0.0	0.312	20 BL
4.92	0.0	0.325	20 BL
5.00	0.0	0.322	20 BL
6.99	0.0	0.312	20 BL
5.02	0.0	0.147	10 BL
5.04	19.8	0.140	10 BL
5.04	50.7	0.141	10 BL

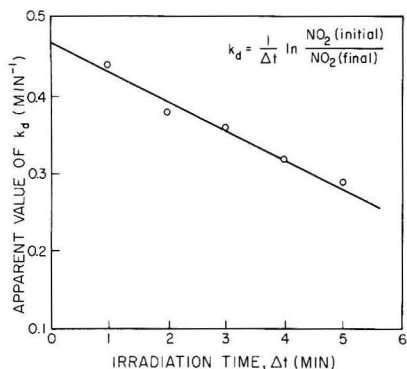


Figure 4. Variation of apparent value of k_d with irradiation time using Equation 2

20 black light fluorescent lamps, and fixed NO₂ and varying NO using 10 lamps. The estimated value of k_1 is a constant in each case, values of k_1 differing only because the uv intensity was different for the two sets of experiments. The estimated value of k_1 for 10 lamps (av 0.143 min⁻¹) is in excellent agreement with the experimental value of k_1 (0.144 min⁻¹) shown in Figure 2 determined by reducing the pressure of the system.

Discussion of the Experimental Results. A study has recently been published (Laity, 1971) comparing black light fluorescent lighting to natural sunlight for several synthetic smog mixtures. No significant difference in the rates of reaction or in the products was found, thus further establishing the usefulness of the NO₂ photolysis method of measurement of light intensity.

Dimitriadis (1970) reported that the temperature of black light fluorescent lamps must be carefully controlled if their ultraviolet output is to remain constant. Most lamps yield maximum uv at an ambient temperature of about 70°F (22°C). Our experience indicates that a rise of 30°F in the temperature of the air surrounding the lamps results in a 40% decrease in uv output, as measured by a photoresistor sensitive to light in the 300–400 nm range. Moreover, some lamps exhibit a warm-up period of several minutes over which the intensity gradually increases to the maximum value. It is important that the light intensity be constant or at least well defined during the k_1 mea-

surement. This may not be the case if the lamps are switched on to initiate photolysis. The lamps used in this study achieved constant intensity immediately.

Algebraic analysis of Equation 4 allows one to deduce values of R_1 , R_2 , and R_3 , but not of the individual rate constants contained in these terms. Our values of these terms along with those of Schuck et al. (1966) are shown below:

Rate— constant ratio	This work	Schuck et al. (1966)
R_1	0.27	0.33
R_2	0.16	0.18
R_3	Not determined	0.00115

The concentration range investigated in this study is the most useful for k_1 studies in environmental chambers. Much additional work has been conducted at higher NO₂ pressures (ca. 1000 ppm) in the past. The results of these earlier studies are not conclusive and the mechanism for photolysis at these higher concentrations is not satisfactorily established. It is probable that reactions not included in the Ford-Endow mechanism are important at higher NO₂ partial pressures. For example, photoexcited states of NO₂ produced by radiation of wavelength greater than about 385 nm (the midpoint of the dissociation region) are important at higher NO₂ concentrations. However, we have estimated the contribution from these processes at the NO₂ pressures used in this work and find it to be negligible as a result of rapid collisional deactivation by N₂.

Finally, we wish to stress that the use of k_d rather than k_1 should henceforth be avoided in all light intensity determinations. Figure 4 shows the apparent value of k_d as a function of Δt where Equation 2 has been approximated by

$$k_d = \frac{1}{\Delta t} \ln \frac{[\text{NO}_2]}{[\text{NO}_2]_0}$$

When determined by this formula, k_d varies strongly with Δt , particularly at k_1 values typical of normal bright noonday sun in Los Angeles (about 0.4 min⁻¹) (Nader, 1967). The error in assuming that the NO₂-time curve is linear for even a few minutes is quite significant. The determination of k_1 from Equation 7 eliminates the need to extrapolate the curve to zero time and provides a direct means of calculation k_1 .

Effect of O₂ on NO₂ Photolysis in N₂

The above experimental results have been obtained for a system initially free of O₂. Often there may exist small amounts of O₂ as an impurity in the N₂ or as a result of inadequate purging of the chamber. It is of importance, therefore, to assess the effect of the presence of O₂ on the value of k_1 calculated from Equation 7 assuming no O₂ is present. In Table III, we show the effect of initial O₂ concentration on the calculated value of k_1 from Equation 7, assuming no O₂ is present. We see that up to 20 ppm, the presence of O₂ has little effect on the calculated value of k_1 at $k_1 = 0.4$ min⁻¹. We recommend, therefore, that experimenters use a grade of N₂ containing below 20 ppm of O₂ or take precautions to remove O₂ before performing the NO₂ photolysis. For those O₂ concentrations for which Equation 6 is valid, Equation 6 can be used directly to compute k_1 from NO₂ vs. time data when O₂ is present.

Table III. Effect of O₂ on the Calculated Value of k₁ from Equations 6 and 7 (Actual value of k₁ = 0.4 min⁻¹)

[O ₂], ppm	0	20	50	100	200	500	1000
Apparent value of k ₁ , min ⁻¹ , Equation 6	0.38	0.38	0.38	0.38	0.39	0.41	0.44
Apparent value of k ₁ , min ⁻¹ , Equation 7	0.38	0.37	0.35	0.33	0.29	0.23	0.18

To assess the validity of Equation 6, we have compared the predicted k_1 values from Equation 6 with the actual value of 0.4 min^{-1} as in Table III, as obtained by a numerical solution of the mechanism in Table I. We see that Equation 6 is valid up to about 1000 ppm of O_2 , at which point the assumption that O_3 is in steady state begins to be in error. We note that the data from which k_1 has been calculated were obtained by numerically integrating the mechanism in Table I using the rate constants in Table I, whereas the calculated values of k_1 from Equations 6 and 7 were obtained using the experimentally obtained values of R_1 and R_2 . This accounts for the discrepancy between the actual and calculated k_1 values at 0 ppm of O_2 .

Photolysis of NO_2 in air has been considered by Bufalini and Stephens (1965). Because of several experimental problems, such as removing water, CO, and hydrocarbon impurities present in air, this represents a less desirable means of computing k_1 than does NO_2 photolysis in N_2 .

Conclusions

As a result of this study we recommend that the fictitious parameter k_d henceforth be abandoned as a measure of the light intensity in a smog chamber in favor of k_1 , the absolute photolysis rate of NO_2 . The data needed to calculate k_1 from the irradiation of NO_2 in N_2 by Equation 7 are no different from those previously used to calculate k_d , so that the experimental technique remains unchanged. We have demonstrated the feasibility of using this method in the ranges of 1–7 ppm of NO_2 and 0–50 ppm of NO.

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Selective Electrode Measurement of Ammonia in Water and Wastes

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■ The use of an ammonia selective electrode in the determination of ammonia in surface waters, sewage samples, and saline waters was investigated. The electrode exhibited Nernstian behavior at a minimum concentration of 0.02 mg $\text{NH}_3\text{-N/l.}$ in distilled water and 0.03 mg $\text{NH}_3\text{-N/l.}$ in actual samples. When the values obtained for river and sewage samples were compared to those from the indophenol blue method on a Technicon AutoAnalyzer, the results differed by an average of 1.2% and 4.6%, respectively. On river water samples, the known addition method was tested against direct measurement (use of a calibration curve) and found to be acceptable. In addition to being inexpensive, the ammonia electrode offered the advantages of minimal sample and reagent preparation prior to analysis, wide concentration range, precision and accuracy comparable to accepted methods, and speed (maximum of 5 min per sample).

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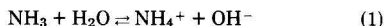
The Analytical Quality Control Laboratory (AQCL) of the National Environmental Research Center, Environmental Protection Agency (EPA), Cincinnati, Ohio, has as its mission the development of physical, biological, and microbiological methods for the field and laboratory analysis of water, waste water, and sediment samples. Additional responsibilities include the evaluation of method reliability and the establishment of quality control techniques for EPA laboratories.

At the present time, the two recommended methods for determining ammonia are a manual distillation followed by a colorimetric or titrimetric analysis and an automated indophenol blue procedure, done on a Technicon AutoAnalyzer (EPA, 1971).

Recently, a new ammonia selective electrode was introduced by the Orion Research Inc., Cambridge, Mass. The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode internal solution. This membrane prevents ionic species from entering the internal solution, thus eliminating any false response due to dissolved ions. However,

high levels of ions can affect the solubility of ammonia to some degree and must be removed by dilution.

Dissolved ammonia in the sample solution diffuses through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. In any given sample, the partial pressure of ammonia will be proportional to its concentration. Ammonia diffusing through the membrane dissolves in the internal filling solution and, to a small extent, reacts reversibly with water in the filling solution:



The relationship between ammonia, ammonium ion, and hydroxide ion is given by the following equation:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \text{equilibrium constant} \quad (2)$$

The internal filling solution contains ammonium chloride at a sufficiently high level so that the ammonium ion concentration can be considered fixed. Thus:

$$[\text{OH}^-] = [\text{NH}_3] \times \text{Constant} \quad (3)$$

The potential of the electrode sensing element (with respect to the internal reference element) varies in a Nernstian manner with changes in the hydroxide level: $E = E_0 - S \log [\text{OH}^-]$ where S is the Nernstian slope. Substitution in the above equation shows that the electrode response to ammonia is Nernstian: $E = E_1 - S \log [\text{NH}_3]$. The internal reference element, a single junction type, is the same one used in the Orion chloride selective ion electrode. It senses the fixed level of chloride in the ammonium chloride internal filling solution, thereby acting as a

reference electrode for the sensing element (Orion Research, Inc., 1971).

This study was undertaken to ascertain the feasibility of adapting the electrode to ammonia determinations in surface waters, waste waters, and saline samples. Precision, accuracy, electrode characteristics, extent of application, and comparison to an approved indophenol blue method were thoroughly examined.

Procedure

Equipment. The electrode was an Orion Model 95-10 Ammonia Electrode, incorporating an internal reference electrode and a diffusion-type membrane. An Orion Model 801 digital pH meter, coupled to a Model 851 digital printer, was used to measure the electrode potential. A magnetic stirrer, thermally insulated so as to prevent heating effects from the stirring motor, was used to stir the sample uniformly. An automatic pipet delivered 1-ml aliquots of sodium hydroxide.

Reagents. Water. As a precaution to remove any traces of ammonia, all solutions were made using distilled water that had been run through a Millipore Super Q water purification system, which passes distilled water through a prefilter, a carbon filter, a mixed-bed ion exchange column, and an 0.2- μ filter.

Standard Ammonium Chloride. Analytical reagent grade NH_4Cl was dried at 100°C for 3 hr. A 1000-mg $\text{NH}_3\text{-N/l.}$ standard solution was made by dissolving 3.819 grams in 1.0 liter of Super Q distilled water. This solution was stable for at least one month.

Analytical Procedures. To accommodate the electrode, it is convenient to use 100-ml beakers, which have been thoroughly rinsed several times with Super Q distilled water. At least 70 ml of sample is needed to sufficiently immerse the electrode and at the same time allow for proper stirring. One milliliter of 10*N* sodium hydroxide is added to the sample, which is then placed onto the stirrer. Immediately, the electrode is placed into the sample, making certain no air bubbles are trapped on the membrane of the electrode. There should be no delay after the sodium hydroxide is added, for ammonia may be lost to the air from a stirred solution. When the electrode equilibrates, a reading is recorded. At this point, if the standard addition method is employed, a standard of appropriate concentration is added to the sample and the new reading is recorded. The electrode is rinsed with distilled water between samples and blotted with a dry tissue.

Table I. Ammonia Concentration vs. Electrode Potential at 25°C

Concn of standard, mg $\text{NH}_3\text{-N/l.}$	Absolute potential, mV	Concn measured, mg $\text{NH}_3\text{-N/l.}$
2.0	-21.0	2.06
1.0	- 3.3	1.00
0.5	14.3	0.49
0.2	38.3	0.19
0.1	53.8	0.099
0.05	69.1	0.053
0.03	83.4	0.029

Table II. Ammonia Measurements in River Water Samples

Station	Month	Electrode method, mg $\text{NH}_3\text{-N/l.}$	Automated indophenol blue method, mg $\text{NH}_3\text{-N/l.}$	Differences	
				Mg $\text{NH}_3\text{-N/l.}$	%
A	1	0.280	0.273	+0.007	+2.6
	2	0.375	0.365	+0.010	+2.7
B	1	0.197	0.188	+0.009	+4.8
	2	0.152	0.140	+0.012	+8.6
C	1	0.228	0.235	-0.007	-2.9
	2	0.203	0.187	+0.016	+8.6
D	1	0.207	0.207	0	0
	2	0.172	0.178	-0.006	-3.4
E	1	0.187	0.179	+0.008	+4.5
	2	0.142	0.140	+0.002	+1.4
F	1	0.166	0.169	-0.003	-1.8
	2	0.122	0.159	-0.037	-23.3
G	1	0.394	0.414	-0.020	-4.8
	2	0.111	0.112	-0.001	-0.9
H	1	0.039	0.031	+0.008	+26.0
	2	0.030	0.047	-0.017	-36.0
I	1	0.269	0.273	-0.004	-1.5
	2	0.193	0.206	-0.013	-6.3

Results

Electrode Characteristics. The electrode exhibited a Nernstian response over the range of 0.02-2.0 mg $\text{NH}_3\text{-N/l.}$ with a slope of approximately 59 mV per decade concentration at 25°C (Table I). Care was taken to ensure that the standards and samples were at the same temperature, for there is a 1% change in concentration per degree Centigrade. The minimum detectable concentration in distilled water was 0.02 mg $\text{NH}_3\text{-N/l.}$; in actual samples, 0.03 mg $\text{NH}_3\text{-N/l.}$ The electrode reached equilibrium within 30 sec at a concentration of 1.0 mg $\text{NH}_3\text{-N/l.}$ As the concentration decreased, the response time increased to a maximum of 5 min at 0.02 mg $\text{NH}_3\text{-N/l.}$ Therefore, for purposes of automation of river water samples, a 5-min measuring time could safely be adopted.

Surface Water Samples. Samples from nine stations on the Ohio River and its tributaries were analyzed for their ammonia concentration during March and April 1972. Results from the indophenol blue method on a Technicon AutoAnalyzer were used for comparison with those obtained by the electrode. In each method, two du-

Table III. Ammonia Measurements in Sewage Samples

Sample (dilution)	Electrode method, mg NH ₃ -N/l.	Automated indophenol blue method, mg NH ₃ -N/l.	Differences	
			Mg NH ₃ -N/l.	%
A (1:10)	0.758	0.824	-0.066	-8.0
B (1:10)	0.699	0.723	-0.024	-3.3
C (1:10)	0.641	0.666	-0.025	-3.7
D (1:2)	0.649	0.663	-0.014	-2.1
E (1:2) ^a	0.836	0.890	-0.054	-6.1

^a Sample D spiked with 0.2 mg NH₃-N/l.

plicates and two spikes were included as a quality control measure. From the calculated recovery of spike, the final corrected concentration of ammonia was obtained. The average recovery for the electrode was 98%, the indophenol blue 106% in each run. As seen in Table II, very good comparison was obtained between the two methods. In only one case (sample F-2) did the difference exceed 3 times the standard deviation (0.024) for the indophenol blue method at that level. Also, at low levels, <0.04 mg NH₃-N/l., (samples H-1 and H-2), a large difference was noted in the methods. At these levels, the electrode is very near its detection limit and a small change in the potential reading results in a large concentration error.

Sewage Samples. Samples of sewage from different points (influent, settling tanks, postsettling tanks) of the Mill Creek Sewage Treatment Plant of the Metropolitan Sewer District, Cincinnati, Ohio, were diluted and analyzed by both methods. Quality control was again accomplished by running duplicates and spikes. The concentrations shown in Table III were corrected from the recoveries of the methods. Again, the electrode proved to be a reliable measure of the ammonia content of the sewage samples. There seemed to be no interferences present. In order to analyze the samples by the indophenol blue method, a dilution had to be performed; this was not necessary with the electrode.

Saline Waters. A representative seawater sample was spiked with varying amounts of ammonium chloride in order to investigate the ability to recover ammonia in a saline environment. The value of the blank was subtracted as background from each of the spiked solutions. As shown in Table IV, the mean recovery was 97.1%, which was in keeping with the 98% recovery with the river water samples.

Precision and Accuracy. To test the precision of the electrode, seven replicates at four different concentrations were run in the following order: high, low, high intermediate, and low intermediate (EPA, 1972). The concentrations were obtained from river water samples used either full strength or diluted to yield the needed concentration.

The precision, expressed as standard deviation was ±0.038 at 1.002 mg NH₃-N/l., ±0.003 at 0.132 mg NH₃-N/l., ±0.017 at 0.768 mg NH₃-N/l., and ±0.007 at 0.188 mg NH₃-N/l. This is excellent precision over the concentration range normally found in river waters.

For comparison, the precision of the indophenol blue method at the same concentration levels was ±0.040, ±0.008, ±0.030, and ±0.009 mg NH₃-N/l., respectively. The electrode was comparable to the indophenol blue method in precision and, in fact, was a small degree more precise.

The accuracy of the electrode was tested by running two series of seven spiked replicates at two different concentration levels, and from this calculating the percent recovery. The low and low intermediate river water samples from the precision determination were spiked with 0.20 and 0.50 mg NH₃-N/l., respectively. As seen in Table V, the accuracy of the electrode was equal to that of the indophenol blue method at comparable concentration levels.

Known Addition. To determine if any significant difference existed between the known addition and direct measurement procedures, one set of river water samples was determined utilizing both techniques. With the known addition method, the need to run a standard calibration curve is eliminated, which in turn avoids a requirement that the samples and standards have the same

Table V. Accuracy of the Ammonia Electrode

Method	Concn of sample, ^a mg NH ₃ -N/l.	Concn of spike added, mg NH ₃ -N/l.	Concn of sample + spike, mg NH ₃ -N/l.	Recovery, %
Electrode	0.188	0.50	0.659	96
	0.132	0.20	0.301	91
Indophenol blue	0.224	0.50	0.674	93
	0.163	0.20	0.340	94

^a Mean of seven replicates.

Table IV. Ammonia Measurement in Saline Waters

Concentration of spike added, mg NH ₃ -N/l.	Concentration of spiked sample, ^a mg NH ₃ -N/l.	Recovery, %
0	0.027	...
0.030	0.052	83.3
0.050	0.079	104.0
0.080	0.109	103.0
0.100	0.131	104.0
0.200	0.215	94.0
0.500	0.500	94.6
		97.1 Mean

^a Specific conductivity of sample was 38,800 μmhos (approximately 20,000 mg Cl⁻/l.).

Table VI. Direct Measurement and Known Addition Comparison

Sample	Direct measurement, mg NH ₃ -N/l.	Known addition, mg NH ₃ -N/l.	Difference	
			mg NH ₃ -N/l.	%
A	0.367	0.376	+0.009	+2.5
B	0.146	0.145	-0.001	-0.7
C	0.198	0.201	+0.003	+1.5
D	0.168	0.167	-0.001	-0.6
E	0.137	0.134	-0.003	-2.2
F	0.122	0.118	-0.004	-3.3
G	0.112	0.114	+0.002	+1.6
H	0.026	0.032	+0.006	+23.0
I	0.191	0.198	+0.007	+3.7

ionic strength and temperature. However, the slope at which the electrode is operating and the concentration of ammonia in the sample (within a factor of 10) must be known. As can be seen from Table VI, the two procedures gave comparable results and were interchangeable.

Automation. With certain provisions, the ammonia electrode can be adapted to automatic analysis. The major drawback is that some provision must be made for the addition of sodium hydroxide just prior to presentation of the sample to the electrode. This was overcome by using the ammonia electrode in conjunction with a Beaker Butler (FWPCA, 1970), an instrument for automating ion selective electrode analyses. The Beaker Butler was modified to provide for sodium hydroxide addition just prior to electrode immersion. Using a 5-min sampling period, acceptable results were obtained with standard solutions in distilled water.

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Collection and Determination of Sulfur Dioxide Incorporating Permeation and West-Gaeke Procedure

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■ A method to measure average pollutant concentrations directly for a desired study period has been developed for sampling and determining sulfur dioxide in the ambient atmosphere. Sampling is accomplished by the permeation of the SO₂ through a silicone membrane. The permeated pollutant is trapped and stabilized as dichlorosulfite-mercurate(II) and is subsequently determined by the West-Gaeke procedure. Sampling pumps are not required because permeation is a physical phenomenon which occurs freely. Measured sample volumes are not required because rate of permeation is proportional to concentration. There are no known significant interferences; the procedures are simple and straightforward; the results are comparable with those obtained with present monitors; and the only equipment required, other than a spectrophotometer or filter photometer, is a permeation device costing less than \$50. Because the analytical values relate to state or federal standards without recourse to statistical or other special mathematical study, the method is ideally suited for monitoring applications.

Federal as well as most municipal and state regulations that have been promulgated to establish ambient air quality standards for sulfur dioxide stipulate average concentrations for specified intervals of time. For example, the federal code requires that the average daily concentration must not exceed 365 $\mu\text{g}/\text{m}^3$ for more than one day during a year and the average concentration for that year must not exceed 80 $\mu\text{g}/\text{m}^3$ ("Federal Register," 1971). There is an obvious need for a direct, simple, and reliable method for determining average concentrations, whether it be for 12- or 24-hr periods or for a seven-day or even a 30-day average. Such a method has now been developed.

The approach employs a sampling device based on the permeation principle and an analytical finish based on the West-Gaeke procedure for determining sulfur dioxide.

Most determinations of sulfur dioxide for air pollution monitoring require the use of relatively expensive equipment which uses a colorimetric method such as the West-Gaeke procedure (West and Gaeke, 1956), a coulometric measurement, or possibly a conductometric determination made on samples that are continuously pulled through the apparatus for appropriate treatment and measurement. Alternatively, a gas chromatographic or flame photometric procedure may be used. Each sampling represents an investment of thousands of dollars necessary for equipment. The final processing of data to obtain values for average concentrations of pollutant requires further investment in time and talent. A simple approach that has been often used is the deployment of lead peroxide candles or sulfation plates, which serve as low-cost substitutes for the sophisticated but expensive SO₂ monitors. Unfortunately, the lead peroxide candles do not measure concentration but instead give a measure only of the relative insult due to sulfur dioxide. They represent an "effects method" giving information somewhat similar to that obtained by corrosion coupons used in establishing the relative corrosiveness of the ambient atmosphere. The lead peroxide candle method suffers further because the final determination is based on the measurement of resultant lead sulfate, and this requires a relatively tedious turbidimetric, gravimetric, or colorimetric analysis.

A new method is now proposed which is simple, low in cost, essentially free of interferences, requires no complicated apparatus or availability of power, and may be employed for sampling times as short as 6 hr or as long as a week or more. Of special significance is the fact that this new method provides "integrated" values directly; therefore, average concentrations are provided for each expo-

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sure period and thus relate directly to federal or state standards. The present method utilizes a permeable membrane to collect the sample at a rate proportional to concentration. The permeated sulfur dioxide is captured and stabilized in sodium tetrachloromercurate(II) with the subsequent determination being carried out by the West-Gaeke procedure.

Recommended Procedure

Apparatus. Any suitable spectrophotometer or filter photometer for measurement of absorbance at 575 nm may be used.

Preparation and Calibration of Permeation Device. The permeation device (Figure 1) is prepared by sealing a disk of single-backed dimethyl silicone rubber polymer (General Electric Co., One River Road, Schnectady, N.Y. 12305) to an 8-cm column of 41-mm o.d. glass tubing using silicone rubber cement. The device is then inserted in a rubber stopper as shown in the figure. The membrane backing should be on the exterior of the finished device.

Place 10 ml of 1M sodium tetrachloromercurate(II) in the permeation device. Expose to a known concentration of sulfur dioxide for an appropriate time—typically 3000 $\mu\text{g}/\text{m}^3$ for 2 hr—making sure that less than 2% of the sulfur dioxide in the calibration mixture is absorbed by the permeation instruments being exposed. Larger losses of sulfur dioxide can be tolerated by sacrificing calibration accuracy. The constant, k , is then calculated from the following equation:

$$k = \frac{Ct}{w} \quad (1)$$

where

k = constant, usually in the order of $10^3 \text{ hr}/\text{m}^3$

C = concentration of sulfur dioxide, $\mu\text{g}/\text{m}^3$

t = time, hr

w = amount of sulfur dioxide absorbed, μg

It should be noted that ideally, k should be measured at temperatures corresponding in general to the average temperatures anticipated for the ambient atmospheres in which the device will be used. A calibration chamber such as shown in Figure 2 may be used to expose the permeation device to known concentrations of sulfur dioxide for calibration. It consists of a large chamber through which the sulfur dioxide-air mixture is passed and side tubes into which one or more permeation devices can be introduced. The tube of the permeation device, inserted into a one-hole rubber stopper, is placed in a port of the exposure chamber to make an air-tight seal. Standard sulfur dioxide-air mixture is then introduced by running a known amount of dry, uncontaminated air over a standard permeation tube (O'Keeffe and Ortman, 1966; Scaringelli et al., 1967a) which emits sulfur dioxide at a constant rate. Laboratory air is pumped through activated charcoal and silica gel and over the permeation tube and finally, to the exposure chamber to provide the pure dry air necessary for calibration of the permeable membrane. The purpose of the activated charcoal column is to remove pollutants, including sulfur dioxide, that may be present in the laboratory. The silica gel columns are used to dry the air. The standard permeation tube must be in a dry atmosphere for gravimetric calibration because moisture may be absorbed by the Teflon of the standard tube or by the liquid sulfur dioxide inside the tube and so introduce error. The permeation tube should be maintained at $\pm 0.05^\circ\text{C}$ during the calibration process.

Reagents and Solutions. All reagents and chemicals used should be reagent grade. High-quality deionized water or chlorine-free distilled water should be used for preparing solutions. It is especially important that no free

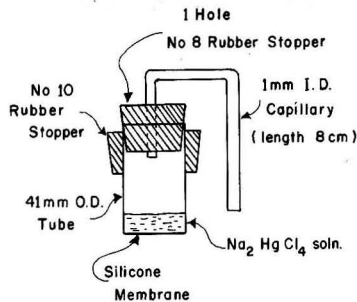


Figure 1. Permeation device

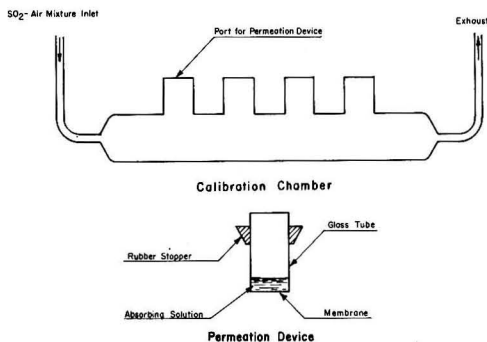


Figure 2. Calibration chamber

chlorine be present in solutions involved in the final SO_2 measurements made by the West-Gaeke procedure.

Sodium Tetrachloromercurate(II) Solution. To make 1M sodium tetrachloromercurate(II) solution, 1 mole (272 grams) of reagent grade mercuric chloride (Mallinckrodt Chemical Works) and 2 moles (117 grams) of sodium chloride (Mallinckrodt Chemical Works or Matheson Coleman and Bell) are dissolved in deionized water and diluted to 1 liter.

Pararosaniline Hydrochloride Solution. This solution may be obtained from Kem-Tech Laboratories, Inc., Baton Rouge, La., in a concentrated form. A solution approximating this concentrate can be prepared by dissolving 0.32 grams of pararosaniline hydrochloride (Fisher Scientific Co., No. p-389) in 240 ml of concentrated hydrochloric acid and diluting to 1 liter with water. Twenty-five milliliters of the reagent concentrate are diluted to 100 ml with water. This resulting solution is stable for at least three months. The concentrate is stable for at least a year. The use of impure pararosaniline may result in high reagent blanks. Blanks of approximately 0.01 absorbance unit should be obtained for 1-cm cells if the reagent is of acceptable quality.

Formaldehyde, 0.2%. Dilute 0.5 ml of 37% formaldehyde (Mallinckrodt Chemical Works) to 100 ml with deionized water. This solution should be prepared daily.

Sampling. Add 10 ml of 1M sodium tetrachloromercurate(II) solution to the permeation device. Expose the device to the ambient atmosphere in an enclosure that allows free movement of air but eliminates direct sunlight (Figure 3). Normal exposure periods vary from 6 hr to 7 days as determined by applicable regulations. If more than half of the solution evaporates during the exposure

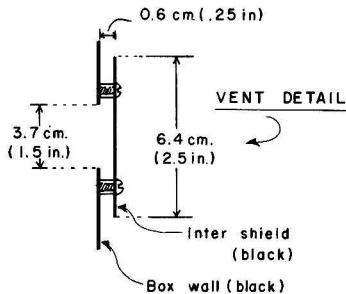
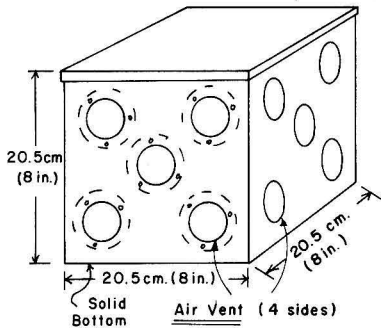


Figure 3. Exposure chamber. Mounting bracket for holding permeation device not shown

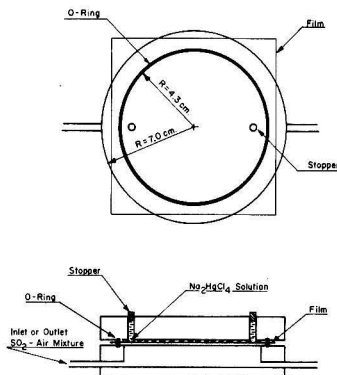


Figure 4. Permeation cell assembly

period, the loss should be made up with deionized water. The same permeation unit may be used repeatedly unless the membrane turns yellow or brown from exposure to excess hydrogen sulfide.

Analysis. Adjust the volume of the trapped sample to 10.0 ml by adding an appropriate amount of deionized water. Add 1 ml each of the pararosaniline and formaldehyde solutions. Read the absorbance at 575 nm after 40 ± 10 min and find the total μg (w) of sulfur dioxide in the solution from a calibration plot. Calculate the average concentration, C , of sulfur dioxide in air for the sampling time, t , using the equation

$$C = \frac{wk}{t} \quad (2)$$

where k is the permeation constant as determined by calibration.

Experimental

Selection of Membranes. Because of the limited data available on the permeability of sulfur dioxide (Brandrup and Immergut, 1966; General Electric Bulletin, 1970), an investigation was initiated to find potentially useful polymer membranes. Various types of membranes were placed on tubes or in the cell assembly shown in Figure 4 and exposed to sulfur dioxide using duplicate samples of all films except those of Teflon. These experiments and later ones dealing with the temperature effect on permeability were carried out with dry air-sulfur dioxide mixtures. Humidity effects were eliminated that might occur during changing laboratory conditions, and an accurate estimation of the water lost by permeation was made. Other methods could have been used for determining the permeability, but it seemed desirable to maintain conditions as near as possible to those that would occur during atmospheric analyses. By use of these particular permeability measuring arrangements, long-term stability and water loss problems were soon recognized.

The relative permeabilities of various films at 30°C are given in Table I. The permeabilities of cellulose acetate, polyethylene, Iolon, and the silicone films are the highest and therefore most promising. The use of cellulose acetate film was immediately ruled out because it was very permeable to water vapor. During the exposure period of 16 hr, more than half of the water of the absorbing solution was lost. Because it was anticipated that temperature effects would be critical, silicone films, as well as polyethylene and Iolon, were next subjected to study to determine which materials would exhibit the least dependence on temperature variations.

Table I. Permeability of Membranes

Membrane		Exposure		Thickness, $\text{cm} \times 10^4$	Relative permeability ^a
Type	Source	Time, hr	Concn, mg/m^3		
Cellulose acetate	Du Pont	16.3	11.9	25	2.50
TFE Teflon	Du Pont	61.8	11.9	125	0.15
FEP Teflon	Du Pont	61.8	11.9	125	0.22
Mylar A	Du Pont	68.5	3.7	25	0.17
Polyvinyl fluoride	Du Pont	68.5	3.8	25	0.61
Iolon	Du Pont	39.9	10.5	25	1.02
Polyethylene	Packaging aids	40.0	10.5	25	1.00
Silastic	Dow-Corning	10.0	3.5	250	289
Dimethyl silicone (unbacked)	General Electric	5.0	13.2	25	272
Dimethyl silicone (single backing)	General Electric	2.0	.57	25	259
Dimethyl silicone (double backing)	General Electric	5.0	13.2	25	310
Silicone-polycarbonate copolymer MEM-213	General Electric	0.5	63.1	100	80
Silicone rubber	Union Carbide	5.0	13.2	100	347

^a These permeabilities are measured relative to the permeability of polyethylene which is assumed to be 1.0.

Temperature Effect. The effect of temperature on the permeability of the selected films can be seen in Table II. These data were obtained from the linear plots of the reciprocal of absolute temperature vs. the logarithm of permeability for the range of 0–40°C. The Dow-Corning film was omitted from consideration because the available sample was too thick for these permeation studies.

The polyethylene and Iolon films exhibited a permeability increase of about 100% for a 10°C increase in temperature, while the three silicone rubber films exhibited a permeability decrease of about 5% for a 10°C increase. This indicated that the silicone membranes would be far superior where anything but very small variations in temperature are encountered. At this point it was obvious that only silicone rubber films would work satisfactorily as the membrane for the sulfur dioxide measuring device. Because the General Electric membranes were thinner than other available silicone films it was decided to use them in the further investigations.

Humidity Effect on Membrane Permeability. Permeability in many cases is a very humidity-dependent phenomenon (Crank and Park, 1968). However, the sulfur dioxide permeability of the silicone rubber membranes tested here was constant over the range of 0–80% relative humidity.

To prepare sulfur dioxide-air mixtures with relative humidities of 0–80%, two streams of air at the flow rates of 200 and 800 ml/min were mixed. The 200-ml/min stream contained dry air and sulfur dioxide at all times. The 800-ml/min stream consisted of dry air when a relative humidity of 0% was to be produced, and air saturated with water vapor when a relative humidity of 80% was to be produced. An additional study was made with the 80% relative humidity air-sulfur dioxide mixtures by adding chilled sodium tetrachloromercurate(II) solution (2°C) to the tubes instead of adding it at room temperature. Addition of the chilled solution caused condensation of moisture which remained on the membrane for about 1.5 hr out of the 5-hr exposure period. This experiment was added because water on the membrane might induce oxidation of the sulfur dioxide or act as a barrier to the sulfur dioxide before permeation could occur. Fortunately, no change in the permeability was found in any of these studies.

Response Time. Permeation through polymer films is not an instantaneous phenomenon. In fact, in some cases, it takes several hours or even days for a gas to penetrate a membrane. The time between the initial exposure of one side of a membrane to a gas and the start of emission of the gas from the other side is called the time lag. It was important to characterize this phenomenon in the present studies so that the response of the final sulfur dioxide measuring instrument to short-term exposures could be predicted. Fortunately, it was found that the permeation rate for the silicone membrane attained 90% of the steady state value within 10 min, thus eliminating time lag as a significant problem.

Stability of Sulfur Dioxide in Sodium Tetrachloromercurate(II) Solutions. Sulfur dioxide is stabilized in sodium tetrachloromercurate(II) solutions as the very stable dichlorosulfiteomercurate(II) complex (Nauman et al., 1960) which resists oxidation, even by permanganate. The stability of sulfur dioxide in tetrachloromercurate(II) solutions has been measured (West and Gaeke, 1956; Scaringelli et al., 1967b; Scaringelli et al., 1970; Lahmann, 1969; Pery and Tabor, 1962), but only little reference has been made to the effect of temperature or concentration of tetrachloromercurate(II) on the stability of the complex species. It was deemed necessary, therefore, to include a

Table II. Effect of Temperature on Permeability

Type and source	Percentage increase for 10°C increase in temp. ^a
Silicone rubber (Union Carbide)	-6.0
Dimethyl silicone unbacked (General Electric)	-5.2
Dimethyl silicone double backing (General Electric)	-4.9
Polyethylene (Packaging Aids Corp.)	109
Iolon (Du Pont)	99

^a A decrease in temperature would cause a much smaller error for polyethylene and Iolon. For the silicone films a decrease or an increase in temperature causes almost the same error.

Table III. Stability of Sulfur Dioxide in Tetrachloromercurate(II) Solution

Tetrachloromercurate concn, M	Temp, °C	Percentage decay	
		Per 10 days	Per day
0.1	30	21	2.5
0.1 + EDTA	30	22	2.7
0.1	40	74	12
0.1 ^a	40	73	12
0.4	40	42	5.2
1	30	4	0.5
1	40	28	3.0
1 ^b	40	27	2.8
1 + EDTA	40	29	3.7

^a This solution was made with potassium chloride instead of sodium chloride.

^b The starting concentration of sulfur dioxide in this solution was 2 µg/ml rather than 1 µg/ml as in the others.

thorough investigation of the stability of sulfur dioxide in tetrachloromercurate(II) solutions in the present study. A major objective of this investigation was to find a means of enhancing the stability of sulfur dioxide in solution.

The stability of sulfur dioxide in the absorbing solution was studied by maintaining sulfur dioxide-containing sodium tetrachloromercurate(II) solutions at a constant temperature. A sulfur dioxide-air mixture from the permeation apparatus was bubbled through various sodium or potassium tetrachloromercurate(II)-absorbing solutions to obtain desired concentrations of fixed sulfur dioxide. These solutions were then placed in polyethylene bottles which were, in turn, placed in a constant temperature bath. Over an appropriate time period, aliquots of sample were withdrawn and analyzed for sulfur dioxide by the West-Gaeke procedure. Scaringelli et al. (1970) indicated that the sulfur dioxide oxidation reaction is first-order and that it follows the equation

$$\ln C = kt + \ln C_0$$

where

$\ln C$ = natural log of observed concentration

k = rate constant

t = elapsed time

and

$\ln C_0$ = natural log of concentration at time zero

Present studies confirm this first-order reaction plot. Data from these plots are presented in Table III. The percentage of sulfur dioxide oxidized during 1- and 10-day periods is given rather than the slope of the decay curves

Table IV. Field Studies^a

Date	Permeation device	Coulometric	West-Gaeke
6-15-72	<5	<25	<2
6-16-72	<5	<25	<2
6-17-72	<5	<25	<2
6-20-72	156	144	
6-21-72	94	122	
6-22-72	50	46	
6-23-72	31	49	
6-24-72	23	<25	
6-25-72	17	<25	
8-8-72	156		158
8-9-72	74		79
8-10-72	30		28
8-12-72 ^b	132		128
8-13-72	43		47
8-14-72	10		N.D.
8-15-72	<5		2
8-16-72	<5		<2
8-9 to 8-16	42		47
8-17-72	<5		3
8-18-72	6		14
8-19-72	<5		14
8-20-72	120		145
8-21-72	93		99
8-22-72	386		382

^a Industrial area with light to moderate pollution. Temperatures in the mid to low 20's (centigrade) at night and low to mid 30's during the day. Generally sunny days with humidities ranging from 65 to 95%. Winds varied with velocities ranging from light and variable to a high of 15 knots. Concentrations shown are in $\mu\text{g}/\text{m}^3$.

^b Two-day exposure.

so that a better understanding of the relationships between decay and time can be obtained. Scaringelli also indicated that faster decay of sulfur dioxide occurred if the solutions were charged with more than 0.2 $\mu\text{g}/\text{ml}$ sulfur dioxide unless disodium ethylenediaminetetraacetate (EDTA) was added to the tetrachloromercurate(II) solution. Our data show this not to be the case with 0.1M or 1M sodium tetrachloromercurate(II) solutions. It should be noted that Scaringelli used 0.04M potassium tetrachloromercurate(II), which might account for the difference. He also used sulfite rather than gaseous sulfur dioxide. In addition, it can be seen by comparing the data from studies made at 40°C that sulfur dioxide is more stable in the more concentrated tetrachloromercurate(II) solutions. It is probable that the use of solutions more concentrated than 1M would result in further decrease in the decay rate of sulfur dioxide. Because of the gross amounts of mercuric chloride that were necessary even for 1M solutions, it was decided not to pursue this route further and to use 1M solutions in subsequent studies. Also, the rate of decay of 0.5% per day at 30°C must be considered negligible for practical applications, especially in view of the fact that average daily temperatures seldom if ever run this high. At temperatures below 30°C, the decay rate was insignificant.

Exposure to direct sunlight caused the dichlorosulfite-mercurate(II) to decompose rapidly. Therefore, the permeation devices must be protected from solar radiation. This can be accomplished through use of a light-shield mounting box (Figure 1).

A calibration curve using the 1M solution of tetrachloromercurate(II) is linear up to about 8 μg of sulfur dioxide per 10 ml, but deviates from linearity at higher concentrations. The absorbance maximum occurs at 575 nm, color

development reaches a maximum 40 min after addition of reagents, and the analytical range is from 0.1–20 μg .

Influence of Sulfur Dioxide Concentration on Permeability Constant. One might inquire at this point whether the permeability constant does, in fact, apply over the range of concentrations encountered in ambient air. In many cases, such as the permeation of water vapor through cellulose acetate, permeability is not constant. However, for the system of SO_2 and the silicone membrane, permeability varied by less than 8% over the range of 62–3500 $\mu\text{g}/\text{m}^3$ at 23°C, thus confirming the validity of the system as developed.

Interference Studies. Only gaseous pollutants could conceivably interfere with the permeation process. Therefore, interference studies were limited to the more likely potential interferences due to hydrogen sulfide, ozone, and nitrogen dioxide. The effect of these pollutants was studied to determine their influence on permeated and stabilized SO_2 and its subsequent determination. The studies were designed to show any effect that might be related to the sequence of exposure. Thus, exposures of the membrane were made to SO_2 followed by interferant; to interferant followed by SO_2 ; and to interferant plus SO_2 introduced simultaneously.

It seemed reasonable to relate the concentration of the possible interfering gas to the appropriate federal or state standards ("Federal Register," 1971). However, there are no federal standards for hydrogen sulfide concentrations, so reference was made to the recent Texas code (Texas State Dept., 1972) which set a maximum permissible 24-hr average concentration of 15 $\mu\text{g}/\text{m}^3$. Concentrations of 600 $\mu\text{g}/\text{m}^3$ and 4500 $\mu\text{g}/\text{m}^3$, or 20 and 300 times this standard were used for exposure periods of 20 hr. Under these rather harsh conditions, experimental errors of less than 10% were found in all cases. However, the membranes turned light brown during the experiments, and those membranes exposed to 4500 $\mu\text{g}/\text{m}^3$ hydrogen sulfide developed pinhole leaks.

The federal standard for ozone (photochemical oxidants) is 160 $\mu\text{g}/\text{m}^3$ for a 1-hr exposure. A 1-hr exposure to 500 $\mu\text{g}/\text{m}^3$ or three times the standard was used for the interference study; no significant error was observed.

The present federal standard for maximum permissible concentrations of nitrogen dioxide is 100 $\mu\text{g}/\text{m}^3$ (1-year mean). No standard for a shorter time period exists. Assuming that a 24-hr standard would probably be about three times this value, an exposure was made with 300 $\mu\text{g}/\text{m}^3$ of NO_2 . No interference was detected.

Discussion

The primary objective in seeking a new method for determining sulfur dioxide was to provide a utility method that would have the merits of the lead peroxide candle method without its defects. The defects that were most obvious were in the analytical finish and in the inability of the method to relate to pollutant concentration. The analytical finish was considered unsuitable because it involved the use of a tedious and rather difficult gravimetric determination of the sulfate derived from captured SO_2 . The candle method suffered most because it neither measured concentration nor did it measure anything reliably. Wind velocity, humidity, geometry of housing and temperature all were known to affect the rate of sulfation. In spite of their deficiencies, lead peroxide candles or sulfation plates have found wide use because of their very low cost and applicability to multipoint monitoring. In view of the preceding comments, a new or modified analytical approach was sought which would be low-cost, simple, reliable, and directly applicable to the measurement of average SO_2 concentration for selected units of time. Simply

stated, the new method should relate directly to published governmental standards as required for SO₂ monitoring. Such a method was developed, based on sample collection by means of permeation followed by stabilization and determination of collected SO₂ by means of the well-established West-Gaeke spectrophotometric procedure.

The innovative feature of the new method is the sample collection by permeation of the gas, whereby the rate of collection is a direct function of the gas (SO₂) concentration.

Permeation is a process involving the dissolution of a gas at one surface of a membrane, diffusion through the membrane (analogous to diffusion through a liquid), and evaporation (or dissolution) at the other side. In fact, permeation through a polymer film is described mathematically in much the same way as dissolution and diffusion in liquids. A mathematical treatment of permeation is not given here, but it can be noted that in most cases the temperature term is of great significance. However, there are a few cases where a relatively small temperature effect is observed. In general, such examples are found among gases that have large heats of vaporization. Sulfur dioxide is such a gas, and it therefore seemed possible that membranes could be found in which there would be little or no temperature effect on permeability.

Permeability of a membrane, or the permeability constant as it is often called, is described by the equation

$$N = \frac{PA(p_1 - p_2)}{s} \quad (3)$$

where

N = flow rate of gas across the membrane

P = permeability constant

A = area (cm²)

s = membrane thickness

and

$(p_1 - p_2)$ = partial pressure difference across membrane

This constant is, as was explained earlier, usually temperature-dependent. It is obvious from the above equation that the thinner the membrane, the more permeable the membrane becomes. This makes it highly desirable to choose very thin films to promote fast movement of material across the membrane. It was decided, however, not to use membranes thinner than 0.0025 cm (1 mil), since such films would tend to be rather fragile and might also contain pinholes which would allow direct flow of gas or liquid.

An equation can be derived relating the ambient gas concentration to the amount of sulfur dioxide permeated, and absorbed. Appropriate units are assumed where not specifically indicated. Since the partial pressure of sulfur dioxide on the solution side of the membrane is zero, Equation 3 may be rewritten as

$$N = \frac{PAp_1}{s} \quad (4)$$

By multiplying both sides of this equation by the time, t , we have

$$Nt = \frac{PAp_1t}{s} = w \quad (5)$$

where w (μg in 10 ml of solution) is the amount of sulfur dioxide that has penetrated the membrane in time, t , and is absorbed by the 10 ml of absorbing solution. Since the partial pressure is simply a concentration term, p_1 may be conveniently described by the equation

$$p_1 = aC \quad (6)$$

where

C = concentration of sulfur dioxide in the air ($\mu\text{g}/\text{m}^3$)

and

$$a = \text{constant}$$

This expression may be substituted into Equation 5 to give

$$w = \frac{PaCAt}{s} \quad (7)$$

Since p , a , A , and s are constants for a given permeation device, Equation 7 may be presented as

$$C = \frac{wk}{t} \quad (2)$$

where

$$k = s/APa$$

As can be seen, the concentration of sulfur dioxide in air is proportional to the weight of sulfur dioxide absorbed in the sodium tetrachloromercurate(II) solution and inversely proportional to the time of exposure. Therefore, a device having a given membrane configuration may be calibrated by exposing it to sulfur dioxide at a known concentration for a given amount of time.

The validity of the permeation approach and associated spectrophotometric finish has been verified both in the laboratory and in the field. A detection limit of 5 μg of SO₂/m³ has been established, based on twice the variation in the blank which is normally less than ± 0.002 unit. Under laboratory conditions, errors were found to be less than 10% for 24-hr exposure at an SO₂ concentration of 60 $\mu\text{g}/\text{m}^3$. On this basis, the method compares very favorably with present monitoring methods, even those involving sophisticated and costly equipment.

The permeation method was found to be reliable under the stress of changes of relative humidity (0–80%) and temperature (less than 5% error for a 10°C change in normal ranges of temperature). Likewise, possible interferences from hydrogen sulfide, ozone, and nitrogen dioxide proved to be of no significance even when they were present in concentrations of three times the limits established by governmental standards.

As far as could be determined, the most significant parameter determining the reliability of the method was the effect of light. It was noted that exposure to light accelerated the decomposition of the dichlorosulfitemercurate(II) complex. It is imperative that the permeation device be field-mounted to protect it from direct sunlight. Likewise, when the sample is transferred to the laboratory for the spectrophotometric measurement, it should be carefully shielded.

In conclusion it can be stated that a new method has been introduced for the determination of sulfur dioxide in the ambient atmosphere that is low-cost, simple, sensitive, and reliable. The method relates directly to governmental standards for SO₂ monitoring. Of special significance were field tests of the method which demonstrated that comparable results were obtained when the permeation device was mounted in a polluted industrial atmosphere beside SO₂ monitors operating both on the coulometric principle and the West-Gaeke method. Data obtained in the field tests are shown in Table IV.

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Capacity of Ferric Oxide Particles to Oxidize Sulfur Dioxide in Air

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■ The heterogeneous oxidation of sulfur dioxide in air by ferric oxide particles, generated by combustion of iron pentacarbonyl, was investigated, using a Teflon-lined filter-reactor. For the experimental conditions used, the reaction is kinetic controlled. The capacity of ferric oxide particles to oxidize sulfur dioxide in air was found to be 62.6 $\mu\text{g}/\text{mg Fe}_2\text{O}_3$. The reaction rate constant for the heterogeneous reaction was estimated to be $9.4 \times 10^{-3} \text{ ppm}^{-1} \text{ min}^{-1}$. These parameters were not sensitive to either relative humidity or sulfur dioxide concentration. When the capacity is depleted, the average surface coverage with sulfate ions was estimated to be 1.6 ions/100 \AA^2 . The quantity of sulfur dioxide physically adsorbed at 23°C was <0.05 $\mu\text{g}/\text{mg Fe}_2\text{O}_3$. The iron dissolved in the acid formed on the particles ranged from 0 to 1.4 $\mu\text{g}/\text{mg Fe}_2\text{O}_3$.

The adverse health effects, reduction in visual range, and deterioration of materials associated with the oxidation of sulfur dioxide in the atmosphere are well known. The homogeneous gas phase oxidation of sulfur dioxide to sulfur trioxide and subsequent hydration of the trioxide to sulfuric acid; and the heterogeneous gas-liquid or gas-solid oxidation of the dioxide to the acid or sulfate are several reaction mechanisms identified by a number of investigators. The dominant mechanism and rate of oxidation depend on the parameters of the system under consideration.

Davtyan and Ovchinnikova (1955) investigated the heterogeneous oxidation of sulfur dioxide in oxygen, using dry and moistened catalysts (spongy platinum; and Cr_2O_3 , V_2O_5 , ferric oxide, and graphite powder). The quantity of sulfuric acid or sulfate formed approached a limiting value within a few minutes of exposure.

The oxidation of sulfur dioxide in the presence of finely ground powders (sodium chloride, calcium carbonate, Fe_2O_3 , Fe_3O_4 , PbO , PbO_2 , V_2O_5 , CaO , Al_2O_3 , and a mixture of CaO and Al_2O_3), using a static exposure chamber, was investigated by Urone et al. (1968). Appreciable reduction in the concentration of sulfur dioxide in the dark was demonstrated and approximate reaction rates were determined.

An estimation of the quantity of sulfur dioxide sorbed on metal and metal oxide particles has been made by Smith et al. (1969). Aerosols containing particles of Fe_3O_4 , Al_2O_3 , PbO_2 , or platinum in the size range of 0.01 to 0.1 μm were generated by the exploding wire technique.

At room temperature and relative humidities ranging from 43-73%, sulfur dioxide was reported to be chemisorbed on Fe_3O_4 and Al_2O_3 for sulfur dioxide concentrations <2 ppm. For concentrations >2 ppm, chemisorption was followed by physical adsorption.

The rates of oxidation of sulfur dioxide in air on surfaces of solid particles at relative humidities <60% and in droplets at relative humidities greater than the phase transition values were investigated by Cheng et al. (1971), using a Teflon bead plug flow reactor. Micron and submicron size water soluble salt particles (CuCl_2 and NaCl) were exposed to air containing 4-42 ppm of sulfur dioxide. Reaction rates were calculated from the observed decrease in the concentration of sulfur dioxide. At room temperature, reaction rates at relative humidities greater than the phase transition values for the soluble salts were much higher than the reaction rates at relative humidities <60%.

Corn and Cheng (1972) monitored the concentration of sulfur dioxide in a gas stream passing through a plug flow reactor containing insoluble particles. Particles of fly ash, CaCO_3 , and V_2O_5 were ineffective in reducing the concentration of sulfur dioxide while particles of Fe_2O_3 , MnO_2 , activated carbon, and suspended particulates from the air in Pittsburgh were effective in varying degrees.

Some information on the heterogeneous oxidation rate of sulfur dioxide in air is available while, apparently, the capacity of different types of particles to react with sulfur dioxide has not been evaluated. This experimental study was designed to measure the capacity of ferric oxide particles to oxidize sulfur dioxide in air, the reaction rate constant, and the effects of relative humidity and concentration of sulfur dioxide on these parameters. The quantity of sulfur dioxide physically adsorbed on ferric oxide particles was assessed also.

Experimental Apparatus and Procedures

The experimental apparatus used for the generation of ferric oxide particles, the experimental arrangement used for exposing the ferric oxide particles to sulfur dioxide in air, procedures for sampling and analysis, and analytical techniques are described in this section. Ferric oxide particles were generated by the combustion of iron pentacarbonyl vapor in an air stream (Bulba and Silverman, 1966), and deposited as a thin layer on a Teflon-fiber filter. A small flow of nitrogen (6 ml/min) was bubbled through a midjet impinger containing iron pentacarbonyl and maintained at room temperature. The iron pentacarbonyl

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vapor in nitrogen was then mixed with combustion air (2 l./min) and passed through a borosilicate glass tube (1 in. i.d., 2-ft length). An electric muffle furnace connected to a temperature regulator was used to heat the glass tube. The temperature at the center of the tube was maintained at $300 \pm 5^\circ\text{C}$. The ferric oxide particles produced in the heated zone were then mixed with cooling air (17 l./min), passed through a 5-l. flask, and deposited as a thin layer on a Teflon-fiber filter (Mitex, Type LSWP, Millipore Corp.; 90-mm diameter; 125–150 μm thickness; 5 ± 1.5 μm pore diameter; and a pore volume of 80%). The filter was supported by a Teflon-coated stainless steel screen which was housed in the filter-reactor apparatus with all-Teflon interior lining.

The reactor was used as a filter apparatus for the deposition of ferric oxide particles onto the Teflon-fiber filter substrate or as a flow reactor for exposure of ferric oxide particles (deposited on the substrate) to sulfur dioxide in air. A critical orifice located after the filter-reactor apparatus maintained a constant flow rate of 15.4 l./min. Approximately 5 mg of ferric oxide particles were deposited on a circular area of 45.6 cm^2 of the filter in about 10 min. The filter with the deposited particles was then placed in a glass Petri dish and stored in a desiccator until needed.

For size analysis, particles were collected on a carbon-coated $\frac{1}{8}$ -in. diameter copper grid using a thermal precipitator (Thermopositor, American Instrument Co.). The sampling conditions used were an air flow rate of 1 ft^3/hr and a sampling time of 10 sec. Photographs of particles were made using a Hitachi electron microscope (Type HU-11A). A particle size distribution was determined from prints enlarged to 80,000 \times . The geometric mean diameter by count (Feret's diameter) was 0.028 μm and the geometric standard deviation was 1.3.

Surface area of ferric oxide particles was determined (by Micromeritics Instrument Corp.) using the Orr Surface-Area Pore-Volume Analyzer (Model 2100A). The specific surface area determined by the standard multi-point BET technique using nitrogen adsorption was 247 m^2/g .

Analyses for the iron content of the ferric oxide particles using the 1,10-phenanthroline method (Sandell, 1959) showed that 90% of the particles by weight could be accounted for as ferric oxide. Gases adsorbed on the particle surfaces may constitute a substantial fraction of the remainder.

The experimental arrangement for exposing ferric oxide particles to gas mixtures is shown in Figure 1. Air (dry grade) from a compressed air cylinder was purified by passing through an activated charcoal filter and a membrane cartridge filter (Gelman Instrument Co., 0.45- μm pore diameter). The air stream was then divided into two streams. One stream was humidified by passing through a train of four bubblers containing water. The two streams were subsequently recombined. By adjustment of the ratio of flow rates of the two streams, it was possible to obtain relative humidities ranging from 2–3% to 94% at room temperature. Total air flow rates used were either 2.5 or 3.5 l./min. The relative humidity was measured with a wet and dry bulb psychrometer (Atkins Thermistor Psychrometer, Model No. 3Z02B, Atkins Technical Inc.).

Sulfur dioxide from a lecture bottle was metered into the air stream of known relative humidity using an asbestos flow meter (Saltzman, 1961). The main feature of the asbestos flow meter is a three-way, T-shaped, capillary stopcock with one plug tightly packed with asbestos. The rate of sulfur dioxide diffusing through the asbestos plug depends on the packing density of the plug and the pres-

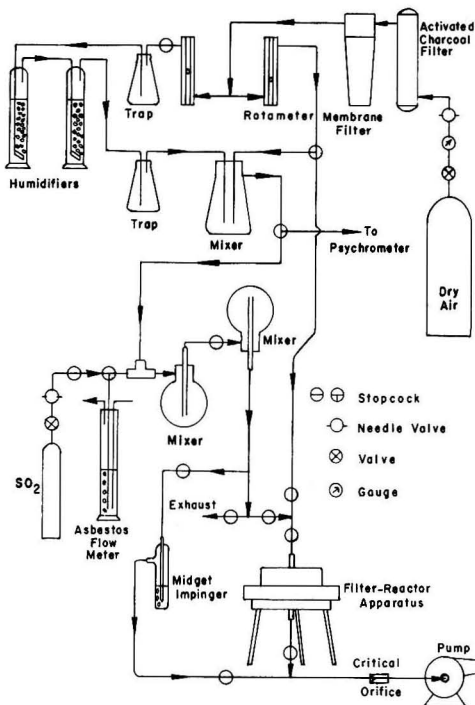


Figure 1. Experimental arrangement for exposure of ferric oxide particles to mixtures of sulfur dioxide in air

sure difference across the plug. The pressure of sulfur dioxide upstream of the plug was maintained constant by discharging sulfur dioxide through the vertical leg of the three-way stopcock. The pressure at this point was maintained at some desired value by submergence of the vertical leg in a column of water saturated with sulfur dioxide. When the height of this water column was varied, it was possible to introduce a few to several hundred μl . of sulfur dioxide per minute into the air stream. The sulfur dioxide-air mixture was passed through two consecutive mixing flasks. The sulfur dioxide concentration of the gas mixture was determined at this point.

The concentration of sulfur dioxide used in this study ranged from about 5–19 ppm and was determined by the modified West and Gaeke method (Scaringelli, et al. 1967).

The quantity of sulfate detected in different control samples were determined by nephelometry. These control or blank samples served to assess the accuracy of the procedures used. The different types of control or blank samples analyzed were Mitex filter without ferric oxide particles and without exposure to sulfur dioxide; ferric oxide particles deposited on a Mitex filter and unexposed to sulfur dioxide; Mitex filter with ferric oxide deposited on its surface and exposed to air for 90 min, using the filter-reactor; Mitex filter without ferric oxide particles and exposed to sulfur dioxide for 90 min, using the filter-reactor; and the wash procedure, using deionized water and glassware associated with the washing procedure. The levels of sulfate found in the various control samples are summarized in Table I. These levels are very close to the estimated sensitivity of the analytical method for sulfate de-

Table I. Sulfate Levels Detected in Different Types of Control Samples

Control samples	Relative humidity, %	Sulfur dioxide concn, ppm	$\mu\text{g}/5 \text{ mg Fe}_2\text{O}_3$	
			Sulfate formed ^a	Average of group
Washing procedure, using deionized water and glassware with the washing procedure			15	
			2	7
			9	
Mitex filter without ferric oxide particles and without exposure to sulfur dioxide			3	
			12	
Ferric oxide particles deposited on a Mitex filter and unexposed to sulfur dioxide			25	13
			3	
			12	
Mitex filter without ferric oxide particles and exposed to sulfur dioxide for 90 min, using the filter-reactor			5	
			20	14
			20	
			16	
			3	
	30	9.4	18	18
	48	10.1	3	
	50	4.7	9	
	50	9.8	24	
	50	9.5	4	
	50	10.0	26	17
	50	10.0	19	
50	10.2	1		
50	18.8	35		
50	9.6	30		
74	9.9	4	10	
75	7.3	15		
94	7.5	14	16	
94	10.3	18		
Mitex filter with ferric oxide deposited on its surface and exposed to air for 90 min, using the filter-reactor	30	0.0	16	16
	50	0.0	18	18

^a Sulfate in μg per 5 mg Fe_2O_3 or in μg per test when ferric oxide is absent. The estimated sensitivity of the analytical method used is 5 μg sulfate when 20-ml aliquots are used.

termination and indicate the degree of extraneous particles which were introduced in the various steps of the procedure. The sulfate levels detected in the different control samples were small and adjustments to measurements were unnecessary. The flow rate of gas mixtures through the flow reactor was maintained constant at either 0.5 l./min or 3 l./min by using a critical orifice between the reactor and the pump. These two flow rates correspond to interstitial gas velocities through the filter pores of 0.22 and 1.3 cm/sec. The corresponding particle Reynolds numbers based on a geometric mean diameter of 0.028 μm were 4.1×10^{-6} and 2.4×10^{-5} and indicate laminar flow conditions.

In order to measure the rate of oxidation of sulfur dioxide and the quantity of sulfate formed, ferric oxide particles deposited on the filter substrate were exposed to gas mixtures for different time intervals ranging from 5 to 90 minutes. Immediately after the exposure, the filter substrate with ferric oxide particles was removed from the filter-reactor and submerged in 50 ml of deionized water in a 600-ml borosilicate glass beaker. The beaker was covered with a watch glass and the content was boiled gently for 90 min. The filter substrate was kept submerged throughout the boiling period using a flat, glass-coil tamper. At the end of the boiling period, the filter substrate was removed and rinsed with about 30 ml of deionized

water. This rinse water was added to the beaker. The water used for extraction and the rinse water were boiled gently until the final volume was reduced to about 25 ml. The content of the beaker was then filtered through a membrane filter (MF-Millipore, Type GS, Millipore Corp.; 47-mm filter diameter; 0.22- μm pore diameter) to remove the ferric oxide particles. The volume of the filtrate was adjusted to 50 ml with deionized water. Analyses of the filtrate for sulfate, dissolved iron, and pH were made. The ferric oxide particles deposited on a Teflon-fiber filter were exposed to the sulfur dioxide-air mixture passing through the reactor.

Sulfate was determined by a modified nephelometric method (Kiley and Rogers, 1955) using a Hach Turbidimeter (Model 1860, Hach Chemical Co.). Soluble iron was determined either by the 1,10-phenanthroline method using a colorimeter (Spectronic 20, Bausch and Lomb) or by an atomic absorption spectrophotometer (maximum versatility, Model 82-500, Jarrell-Ash).

The quantity of sulfur dioxide physically adsorbed on ferric oxide particles was determined by measuring the quantity of sulfur dioxide desorbed from the particles. Desorption was achieved by using 5 liters of dry air (0.5 l./min) to purge the filter-reactor after exposure of the ferric oxide particles to sulfur dioxide-air mixtures for periods ranging from 5 to 90 min. The desorbed sulfur dioxide was collected by bubbling the dry purge air through a bubbler containing potassium tetrachloromercurate.

For a given concentration of the chemical compound being determined, the accuracy was taken to be the maximum deviation of observed values from the line of best fit, using several calibration curves. Generally, the accuracy is in the order of 2-5% of the concentration of the chemical compound being determined. In absolute quantities, the determinations for sulfur dioxide, dissolved iron, and sulfate are accurate to approximately 0.5 $\mu\text{g SO}_2$, 0.5 $\mu\text{g Fe}$, and 5 $\mu\text{g SO}_4^{2-}$, respectively.

Capacity Limited Heterogeneous Reaction

Heterogeneous reaction of sulfur dioxide with metal oxides and other types of particles to form sulfuric acid is recognized as one of several significant mechanisms of acid formation in the urban atmosphere. The catalytic activity of metal oxides, particularly those of the transition metals, is considered an important particulate property in the oxidation of sulfur dioxide. However, at ambient temperatures, the heterogeneous oxidation of sulfur dioxide on surfaces of nonhygroscopic metal oxide particles is not a true catalytic reaction. The active sites on the surfaces of particles become occupied by the products of reaction during the course of the reaction. These active sites are not available subsequently for further reaction, as would be the case in a true catalytic reaction. Hence, the oxidation of sulfur dioxide on the surfaces of ferric oxide particles is expected to form a finite quantity of acid; the quantity being proportional to the number of active sites originally available for reaction. The term "capacity limited heterogeneous reaction" is used here to designate this class of gas-solid reaction.

The capacity limited heterogeneous oxidation of sulfur dioxide on surfaces of ferric oxide particles at room temperature (23°C) may be regarded to consist of the following sequence of steps: (1) chemisorption of oxygen onto the surface sites, (2) diffusion of sulfur dioxide to the surface, (3) reaction between sulfur dioxide and chemisorbed oxygen to form sulfur trioxide, (4) hydration of sulfur trioxide to sulfuric acid, and (5) partial dissolution of ferric oxide by the sulfuric acid.

If step 3 is the rate-controlling step, the rate of sulfate formation can be expressed mathematically as:

$$\frac{d\theta}{dt} = k_1 P \theta_o - k_2 \theta \quad (1)$$

Since the reaction product, SO_3 , is converted to sulfate ions immediately upon hydration in the presence of water vapor, k_2 is taken as zero and Equation 1 becomes:

$$\frac{d\theta}{dt} = k_1 P \theta_o \quad (2)$$

In terms of a specific heterogeneous rate constant, k_1' , Equation 2 is

$$\frac{L}{A} \frac{d\theta}{dt} = 253 k_1' P \theta_o \quad (3)$$

Substituting $(1 - \theta)$ for θ_o in Equation 2, rearranging, and integrating give:

$$\theta = 1 - e^{-k_1 P t} \quad (4)$$

Also,

$$L\theta = L(1 - e^{-k_1 P t}) \quad (5)$$

This description of a capacity-limited heterogeneous reaction is a kinetic-controlled model of the reaction. The model is also predicated on all the active surface sites being equally accessible for reaction. Differentiation of a kinetic-controlled reaction from a diffusion-controlled one is possible on the basis of the dimensionless parameter $\hat{\gamma}_n$,

$$\hat{\gamma}_n \equiv \left(\frac{k_n' C_\infty^{n-1} r_o}{D} \right) \left(\frac{1}{\text{Nu}} \right) \quad (6)$$

For $\hat{\gamma}_n < 10^{-1}$, the reaction is kinetic controlled (Peter- sen, 1965).

Equal accessibility implies that all sites are exposed to

the same concentration of reactant gas at all times. This condition is met when a single layer or a few layers of particles, deposited on a nonreactive filter support, are exposed to air containing a constant concentration of reactant gas which is flowing continuously through the filter.

If the condition of equal accessibility is not met initially, but is met after a finite time period, a convenient form of Equations 3 and 4 for the purpose of calculating the reaction rate constant may be obtained by the substitutions:

$$\theta' = (\theta - \theta_1)/(1 - \theta_1)$$

$$t' = (t - t_1)$$

$$L' = L(1 - \theta_1)$$

Variables with the subscript one correspond to the time when the equal accessibility condition is met. Equations 3 and 4 in terms of the primed quantities become:

$$\theta' = 1 - e^{-k_1 P t'} \quad (7)$$

$$L' \theta' = L' (1 - e^{-k_1 P t'}) \quad (8)$$

Equation 7 may also be written as

$$k_1 = - \frac{\ln(1 - \theta')}{P t'} \quad (9)$$

Results and Discussion

The quantity of sulfate formed on the surfaces of ferric oxide particles exposed to air, using the filter-reactor described previously, was obtained as a function of time. The capacity of the ferric oxide particles to form sulfate and the rate constant for the heterogeneous reaction was determined from these measurements. The effects of relative humidity, sulfur dioxide concentration, and the particle Reynolds number on the capacity and reaction rate constant were evaluated. The quantity of iron dissolved in

Table II. Heterogeneous Oxidation of Sulfur Dioxide in Air ($\text{Re} = 4.1 \times 10^{-6}$)

Experimental series	Sample size, mg Fe_2O_3	Relative humidity, %	Sulfur dioxide concn, ppm	Exposure time, min	Reaction products		
					Sulfate formed, $\mu\text{g}/5 \text{ mg } \text{Fe}_2\text{O}_3$	Dissolved iron, $\mu\text{g}/5 \text{ mg } \text{Fe}_2\text{O}_3$	Wash water, pH
A-1	10.9	3	9.9	90	286	4	...
A-2	5.9	30	9.4	90	394	2	5.3
	6.7			90	299	3	4.1
A-3	10.3	48	10.1	90	325	7	3.8
	10.8			90	328	6	3.8
A-4	5.1	50	9.5	90	351	^a	5.4
	5.5			90	302	5	4.1
A-5	5.1	50	10.0	90	287
	5.4			90	282
A-6	5.1	50	10.2	90	314
	5.0			90	307
A-7	9.5	74	9.9	90	279	3	4.4
A-8	5.5	75	7.3	15	160
	5.4			15	163
	5.3			30	249
	5.6			30	292
	5.1			90	336
	5.7			90	326
	4.8			90	284
A-9	5.6	94	7.5	15	181
	4.9			15	191
	5.0			30	308
	5.9			30	256
	4.9			90	365
	5.0			90	356
	5.1			90	353
A-10	10.3	94	10.3	90	216	4	4.1

^a Less than detectable limit.

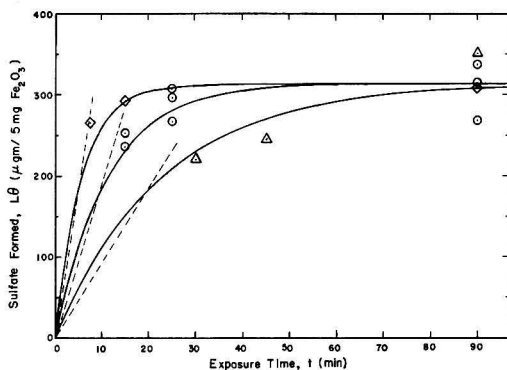


Figure 2. Sulfate formation as a function of time

Sulfur dioxide concentration: \diamond = 18.8 ppm, \circ = 9.6 ppm, and \triangle = 4.7 ppm; relative humidity = 50%; and flow-through velocity = 0.22 cm/sec. Experimental series B-1, B-2, and B-3, respectively

Table III. Heterogeneous Oxidation of Sulfur Dioxide at Different Concentrations of Sulfur Dioxide (Relative Humidity = 50%)

Experimental series	Sample size, mg Fe_2O_3	Sulfur dioxide concn, ppm	Particle Reynolds no.	Exposure time, min	Sulfate formed, $\mu\text{g}/5 \text{ mg } \text{Fe}_2\text{O}_3$
B-1	5.6	18.8	4.1×10^{-6}	7.5	265
	6.2			15	292
	6.0			90	308
B-2	5.5	9.6	4.1×10^{-6}	15	236
	5.5			15	252
	5.5			25	295
	5.3			25	266
	5.2			25	306
	5.6			90	312
	5.6			90	336
5.9	90	267			
B-3	5.7	4.7	4.1×10^{-6}	30	219
	6.2			45	244
	5.7			90	350
C-1	5.9	9.8	2.4×10^{-5}	5	246
	5.7			10	254
	5.2			15	279
	5.8			90	260

the acid formed on the surfaces of the ferric oxide particles was measured. Also, an assessment of the quantity of sulfur dioxide physically adsorbed on the surfaces of ferric oxide particles was made.

The quantity of sulfate formed as a function of time is shown in Figure 2. The data points shown are for exposures of 5-mg samples of ferric oxide particles to sulfur dioxide concentrations of 4.7, 9.6, and 18.8 ppm; and to a relative humidity of 50%. The data for this and five other series of observations are tabulated in Tables II and III. The dashed lines shown in Figure 2 represent the cumulative quantity of sulfate with time which can be formed if all of the sulfur dioxide passing through the filter-reactor were converted to sulfate. The solid curves are theoretical quantities of sulfate formed, based on Equation 9.

During the initial period of the experiments, the quantity of sulfate formed with time is linear and is the same as the equivalent quantity of sulfur dioxide passing through the filter-reactor. During this period, the condition of uniform accessibility is not met since all the sulfur

Table IV. Capacity of Ferric Oxide Particles to Form Sulfate

Experimental series	No. of measurements	Relative humidity, %	Average capacity, $\mu\text{g}/5 \text{ mg } \text{Fe}_2\text{O}_3^a$
A-1	1	3	286
A-2	2	30	346.5
A-3			
A-4			
A-5			
A-6	14	48 to 50	309
B-1			
B-2			
B-3			
C-1			
A-7			
A-8	4	74 to 75	306
A-9	4	94	323
A-10			

^a Average of 25 measurements = $313 \mu\text{g } \text{SO}_4^{2-}/5 \text{ mg } \text{Fe}_2\text{O}_3$.

dioxide passing through the reactor is converted to sulfate. The reaction rate constant cannot be estimated solely from the rate of sulfate formation in this period. However, the reaction rate constant may be calculated with the aid of Equation 9, using data obtained during the subsequent period when the condition of uniform accessibility is essentially met.

Calculation of the dimensionless parameter $\hat{\gamma}_n$ for the conditions of experimental series B-2 (Table III) was made. For experimental series B-2, the condition of uniform accessibility is met for exposure times greater than 20 min. Conditions of the experiment at the reaction time period between 20 and 30 min were a sulfur dioxide concentration of 9.6 ppm, a relative humidity of 50%, and a flow-through velocity of 0.22 cm/sec, 5-mg samples of ferric oxide in the filter-reactor; and the geometric mean particle diameter was 0.028 μm . The particle Reynolds number for these conditions was 4.1×10^{-6} . Measured values of sulfate formation were $\theta_0 = 0.069$ at 25 min and $L\Delta\theta = 25 \mu\text{g } \text{SO}_4^{2-}$. The specific surface area of the particles, as measured by the BET method, is $2.47 \times 10^6 \text{ cm}^2/\text{g}$. Using these values in Equation 3 gave k_1' values of $1.3 \times 10^{-3} \text{ cm}^2/\text{sec}$. For this value of k_1' and $n = 1$, $D = 1.16 \times 10^{-1} \text{ cm}^2/\text{sec}$, and $\text{Nu} = 2$ (applicable when $\text{Re} < 10^{-1}$, Frank-Kamenetskii, 1969), the value of $\hat{\gamma}_1$ was estimated using Equation 6. The value $\hat{\gamma}_1$ was found to be in the order of 10^{-8} which is $\ll 10^{-1}$. The experimental data, thus, indicate that the heterogeneous oxidation of sulfur dioxide on surfaces of iron oxide particles is a kinetic-controlled surface reaction.

The capacity of ferric oxide particles for the formation of sulfate upon exposure of the particles to different sulfur dioxide concentrations ranging from 4.7-18.8 ppm and to a relative humidity of approximately 50% is summarized in Tables II and III. The range of sulfate formed per 5 mg of ferric oxide particles ranged from 260-351 μg . The capacities are not substantially different for the four different sulfur dioxide concentrations used.

The capacity of ferric oxide particles for the formation of sulfate at relative humidities of 3-94% is shown in Tables II, III, and IV. The arithmetic average of 25 measurements of capacity was found to be $313 \mu\text{g } \text{SO}_4^{2-}/5 \text{ mg } \text{Fe}_2\text{O}_3$. The sulfate formed is approximately 6% when compared with the weight of the original particles. The reproducibility of the measurements is good, as indicated by the standard deviation of the capacity for the 25 measurements—i.e., 39 $\mu\text{g}/5 \text{ mg}$. The capacity is substantially

Table V. Reaction Rate Constant for the SO₂-Fe₂O₃ Heterogeneous Reaction

Exptl. series	Sulfur dioxide concn, ppm	Relative humidity, %	* Particle Reynolds no.	t'/60, min	θ' ^a	-ln(1 - θ')	60 k ₁ , ^b ppm ⁻¹ ·min ⁻¹
B-1	18.8	50	4.1 × 10 ⁻⁶	7.5	0.614	0.950	6.8 × 10 ⁻³
C-1	9.8	50	2.4 × 10 ⁻⁵	7.5	0.491	0.675	9.2 × 10 ⁻³
B-2	9.6	50	4.1 × 10 ⁻⁶	10	0.692	1.18	12.3 × 10 ⁻³
A-9	7.5	94	4.1 × 10 ⁻⁶	15	0.700	1.20	10.7 × 10 ⁻³
A-8	7.3	75	4.1 × 10 ⁻⁶	15	0.756	1.41	12.9 × 10 ⁻³
B-3	4.7	50	4.1 × 10 ⁻⁶	15	0.278	0.325	4.6 × 10 ⁻³

^a Average values of *Lθ* in Tables III and IV, and average capacity listed in Table V were used to calculate θ'.

^b Average of six determinations = 9.4 × 10⁻³ ppm⁻¹·min⁻¹.

constant over the range of relative humidity and sulfur dioxide concentration observed. The capacity is not large and can account for only a small fraction of the acid found in urban air under stagnant conditions.

When the capacity of the particles for the formation of sulfate is depleted, the surface coverage of the particle with sulfate ions is approximately 1.6 ions per 100 Å². This estimate was made with the assumptions that the sulfate ions on the particles form a monolayer, that the cross-sectional area of a sulfate ion is 22 Å² (estimated from the method of Emmett and Brunauer, 1937), and using the measured value of particle specific surface area of 247 m²/g (BET method). This surface coverage corresponds to approximately 35% of the surface area. If the external surface of a smooth sphere of 0.028 μm in diameter is covered with a monolayer of sulfate ions, a surface coverage of 4.2 ions per 100 Å² would result. Hence, the surface appears to be sparsely populated with sulfate ions when the capacity for sulfate formation is depleted.

The quantity of iron dissolved in the acid layer formed on the surfaces of ferric oxide particles was measured. After exposure of the particles to sulfur dioxide in air, using the filter-reactor, the particles were washed with 50 ml of demineralized water. The pH of this wash water was measured and tabulated in Table II. Analysis of the wash water for dissolved iron is also tabulated in Table II. The wash water is highly acidic, as would be expected. The dissolved iron range from 0-7 μg/5 mg Fe₂O₃. The observed mole ratio of iron to sulfate formed was approximately 0.03 while the mole ratio of iron to sulfate in the compound ferric sulfate is 0.67.

A method specific for sulfur dioxide was used to assess the quantity of physically adsorbed sulfur dioxide. Measurements of sulfur dioxide physically adsorbed on the surfaces of ferric oxide particles were made after a 90-min exposure of the particles to 9.9 ppm of sulfur dioxide at a relative humidity of 3%. After exposure, the filter-reactor was purged with 5 liters of dry air and the quantity of sulfur dioxide recovered was the same as that contained in the 170-cm³ volume of the filter-reactor prior to purging. Hence, the quantity of sulfur dioxide physically adsorbed on the surfaces of ferric oxide particles is less than 0.05 μg/mg Fe₂O₃—i.e., essentially the same as the accuracy of the analytical method used.

Measurements of sulfate formed as a function of time and Equation 9 permit calculation of a first-order heterogeneous reaction rate constant, *k*₁, for the oxidation of sulfur dioxide on surfaces of ferric oxide particles. As discussed previously, the condition of uniform accessibility is met only after an initial reaction period. Hence, only data obtained after this initial period are useful for estimating *k*₁. The condition of uniform accessibility is satisfied essentially when the difference between inlet and outlet concentrations of sulfur dioxide is generally 20% of the

inlet concentration. The calculated rate constants are tabulated in Table V. The values range between 4.6 × 10⁻³ and 12.3 × 10⁻³ and the average is 9.4 × 10⁻³ ppm⁻¹·min⁻¹. A graphical comparison of the calculated quantity of sulfate formed at different exposure times, using the average rate constant, with experimental values is shown in Figure 2. Generally, the experimental measurements match well with values calculated from the first-order, kinetic-controlled reaction model. However, the degree of accuracy of the calculated-rate constants is not high because of the limitations imposed by the condition of uniform accessibility.

The rate constant does not appear to be correlated with either relative humidity or sulfur dioxide concentration. A comparison of experimental series B-2 with C-1 indicates that the rate constant is not affected by a sixfold change in the particle Reynolds number. This result is expected for Reynolds number <0.1.

In the case of mass transfer from the gas phase to an absorbing sphere, the Nusselt number approaches a constant and limiting value of 2 when the Reynolds number is <0.1 (Frank-Kamenetskii, 1969). For a constant Nusselt number, the mass transfer coefficient β_m is constant for a given combination of particle size and diffusion coefficient of the diffusing gas specie. Diameters of atmospheric particles range between 0.02 and 20 μm; and densities between 1 to 2 g/cm³. At 23°C and atmospheric pressure, the terminal settling velocity, mean thermal velocity, and Reynolds number for atmospheric particles range from 1.4 × 10⁻⁵ to 2.4 cm/sec, 157 to 5 × 10⁻³ cm/sec, and 1.8 × 10⁻¹⁰ to 3.2 × 10⁻², respectively.

For the range of experimental conditions used, the Reynolds number varied between 4.1 × 10⁻⁶ and 2.4 × 10⁻⁵ and is <0.1. The Nusselt number is thus constant and equal to 2; and the mass transfer coefficient applicable to the filter-reactor, as is the case of atmospheric aerosols, is a constant. Hence, the experimental conditions simulate the gas transfer phenomenon and reaction opportunities of particles suspended in air. Naturally, many other important features related to the interactions of complex gas mixtures with particles of complex chemical composition in the urban atmosphere are not simulated, and many significant extensions of our simple investigation are possible.

Nomenclature

- A = total surface area of a given quantity of ferric oxide particles, cm²/5 mg Fe₂O₃
- C_∞ = concentration of reactant as *r* approaches ∞, mol/cm³
- D = diffusion coefficient, cm²/sec
- D_p = particle diameter, cm
- k₁ = forward reaction constant for first-order surface reaction, ppm⁻¹·sec⁻¹ or (10⁻⁶ atm SO₂/atm)⁻¹·sec⁻¹

k_2 = backward reaction constant for the first-order surface reaction, sec^{-1}
 k_n' = heterogeneous reaction rate constant based on the external surface area of smooth spheres, $\text{cm}(\text{mol}/\text{cm}^3)^{1-n}/\text{sec}$
 L = total capacity of a given quantity of ferric oxide particles to form sulfate, $\mu\text{g}/5 \text{ mg Fe}_2\text{O}_3$
 L' = $L(1 - \theta_1)$
 n = order of the heterogeneous reaction
 Nu = Nusselt number for diffusion ($\beta_m r_o/D$)
 P = concentration of sulfur dioxide, ppm
 r = radial coordinate, cm
 r_o = particle radius, cm
 Re = particle Reynolds number ($D_p U/\nu$)
 t = time, sec
 t' = time with origin at t_1 , $(t - t_1)$
 U = flow velocity, cm/sec

Greek Letters

β_m = mass transfer coefficient, cm/sec
 $\hat{\gamma}_n$ = dimensionless parameter ($k_n' C_{\omega}^{n-1} r_o/D \cdot \text{Nu}$)
 θ = fraction of surface sites occupied by sulfate ions or sulfur trioxide molecules at time t
 θ_1 = θ at time t_1
 θ' = $(\theta - \theta_1)/(1 - \theta_1)$
 θ_o = fraction of surface sites occupied by oxygen atoms at time t
 ν = kinematic viscosity cm^2/sec

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Stimulated Biodegradation of Oil Slicks Using Oleophilic Fertilizers

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■ Biodegradation of polluting oil at sea is seriously limited by the scarcity of nitrogen and phosphorus. Since water-soluble sources of these elements would be ineffective in the ocean, oleophilic compounds were screened to serve as fertilizers for oil slicks. A combination of paraffinized urea and octylphosphate promoted oil biodegradation, both in laboratory experiments and in field trials, to an extent that the practical application of this principle to oil cleanup appears feasible. The tested oleophilic fertilizer supplies nutrients to hydrocarbon-degrading microorganisms selectively and, in contrast to nitrate and phosphate salts, it does not trigger algal blooms.

The oceans of the world are currently being burdened by an estimated oil pollution load of 5- to 10-million metric tons per year (Blumer, 1973), and the resulting damage has caused widespread concern. Considerable research effort is being devoted to the prevention and control of oil spills (Joint Conferences on Prevention and Control of Oil Spills, 1969, 1971), but spills continue to occur. Theoretically, spilled oil can be cleaned up by various skimming devices, but prevailing weather conditions seldom allow this approach to succeed. Ignition is rarely feasible, both be-

cause of safety considerations and because of the rapid evaporative loss of the low flashpoint components. The two remaining conventional measures, dispersion or sinking, are essentially cosmetic in nature. They merely render the oil less offensive but, in fact, increase the exposure of marine life to the pollutant and are for this reason best avoided (Blumer, 1973).

A novel approach to the cleanup of spilled oil attempts to stimulate its biodegradation. This process is the major natural mechanism for elimination of oil from the marine environment, but it occurs at a distressingly slow rate. To speed up this process is the ultimate aim of present research projects in various laboratories (*Chem. Eng. News*, 1970). Several commercial microbial inocula are being marketed for the purpose of oil biodegradation but, to date, no controlled studies have been published on the effectiveness of these products.

In the course of our studies on the limiting factors of oil biodegradation in natural seawater, we were impressed by the magnitude of the positive response to the addition of nitrate and phosphate supplements (Atlas and Bartha, 1972a). Seawater contains very low concentrations of nitrogen and phosphorus, and petroleum or petroleum products are also deficient in these essential nutrients. Nitrate and phosphate are excellent sources of these elements as long as the seawater is enclosed in a laboratory flask, but they may be useless or worse when applied in the open ocean. Because of their solubility in water, these salts can be expected to

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separate rapidly from the floating oil causing little or no benefit to oil-degrading microorganisms. In addition, these mineral nutrients may trigger algal blooms and cause eutrophication problems. Application in the open ocean clearly requires the selection of nitrogen and phosphorus sources that physically adhere to the oil slick and benefit oil-degrading microorganisms selectively. This paper describes an effort to find such compounds and to put them to practical use in the stimulated biodegradation of marine oil slicks.

Materials and Methods

Evaluation of Oleophilic N and P Sources. Aliquots of a fresh seawater sample (100 ml), collected in December off the east coast of Sandy Hook, N.J., and containing its indigenous microbial population, were introduced into the flasks of a gas train arrangement described previously (Atlas and Bartha, 1972b). Each flask received 1 ml of Sweden crude oil plus various nitrogen and phosphorus supplements. Sweden crude oil is a paraffinic petroleum and is described in greater detail in a previous publication (Atlas and Bartha 1972b). The additives were initially selected on the basis of their described physical and chemical properties (Stecher, 1968; Weast, 1967-68). The desired properties were low C:N or C:P ratio to assure low BOD; oleophilic property, or the possibility of being rendered oleophilic; likelihood of being biodegradable and of low toxicity; and ready availability at a reasonable price. Compounds that had these attributes were subjected to a preliminary screening as to their behavior in an agitated two-phase system consisting of *n*-hexadecane and H₂O. Compounds that sank or dissolved in the water were excluded. Those that dissolved in the *n*-hexadecane phase or positioned themselves on the hexadecane-H₂O interface were selected for further testing. As sources of nitrogen were added dodecyl urea (Eastman), trimethylenetetraurea (Allied Chemical), and Sun Oil CRNF (a slow-release paraffinized urea agricultural fertilizer, N-content 26.8%, a gift of Sun Oil Co.). As water-soluble control, KNO₃ was used. All of the nitrogen sources were added in amounts to give a final concentration of 10mM N.

Phosphorus was added as octylphosphate, isooctylphosphate (both gifts of Stauffer Chemical Co.) and hexamethylphosphoramide (Aldrich Chemical Co.). As water-soluble control, Na₂HPO₄ was used. The phosphorus sources were added in amounts to give a final concentration of 0.5mM P, except for hexamethylphosphoramide, which was added to give the proper N concentration. The nitrogen sources except for hexamethylphosphoramide were added in combination with either Na₂HPO₄ or octylphosphate. Isooctylphosphate was added in combination with KNO₃. Hexamethylphosphoramide was added alone as a source of both nitrogen and phosphorus. Two types of controls were included: seawater with Sweden crude oil but no other supplements and seawater with each tested combination of nitrogen and phosphorus but without Sweden crude oil. All treatments were done in duplicate.

The gas train apparatus was mounted on a rotary shaker and agitated at 200 rpm. Carbon dioxide-free air was passed through the flasks at the approximate rate of 15 ml/min. Mineralization (conversion to CO₂) of the crude oil was measured in weekly intervals. After four weeks' incubation at 28°C, all flasks were extracted with diethyl ether and the residual oil was measured by gas chromatography (Atlas and Bartha, 1972b). Sterilized controls served to correct biodegradation data for nonbiological losses.

Simulated Field Tests. Because of the prevailing wave action and tidal conditions, it was not feasible to conduct

the experiment in the open sea. Instead, the test was conducted in tanks with flow-through seawater at the Sandy Hook Marine Laboratory. The tests were conducted during the months of May and June in 113-liter aquarium tanks fitted with overflow outlets. Seawater filtered through cotton gauze and crushed sea shells to remove larger suspended particles was flowing through the tanks at the rate of 450 liters per day. An artificial "sea breeze" was created by an electric fan. Glass tubes 5 cm in diameter and 30 cm long were inserted into styrofoam floats as shown in Figure 1. Twenty-four tubes were floated in each of two tanks. Some tubes were closed on their lower ends with a rubber stopper and were poisoned with 1% HgCl₂ to serve as controls for evaporative losses (a). Others were closed with a Visking cellulose dialysis membrane to allow the exchange of ions and gases but to prevent any loss of undegraded oil by sinking (b). A third type of tube was left open (c). Prior to removal for analysis, each type of tube was closed under water by a rubber stopper and was lifted out with its entire contents.

One milliliter of Sweden crude oil was added to each cylinder. Some of the miniature oil slicks received no supplementation. Others were supplemented with either 101 mg of KNO₃ and 7.5 mg of Na₂HPO₄ or with 62 mg of CRNF fertilizer and 7 mg of octylphosphate. Each treatment was tested with both membrane-closed and open cylinders.

Water temperature was measured daily throughout the experiment. Tubes of each type were removed for analysis weekly. The seawater and the residual oil in the tubes were transferred to separatory funnels. The tubes were rinsed with diethyl ether to ensure complete transfer of the oil. The oil was then extracted using two 100-ml portions of diethyl ether. The extracts were combined, dried with anhydrous Na₂SO₄, and the residual oil was determined by gas chromatography (Atlas and Bartha, 1972b).

Algal Growth. The seawater for this experiment was collected in May off the east coast of Sandy Hook, N.J. Aliquots of seawater (150 ml) were added to sterile 1-liter culture bottles (64 × 99 × 299 mm). The seawater aliquots were either left untreated, were supplemented with KNO₃ and Na₂HPO₄, or were supplemented with CRNF and octylphosphate. The nitrogen supplements were added in amounts to give a final concentration of 10mM N. The phosphorus supplements were added to give a final concentration of 0.5mM P. The bottles were incubated flat on their sides under a bank of fluorescent lights (2 F40 cool white fluorescent tubes located 40 cm above the culture bottles; light intensity 220 foot-candles). Algal growth was measured as chlorophyll according to the method of Warburg (Vishniac, 1957). One hundred milliliters of the seawater was used for the chlorophyll assay.

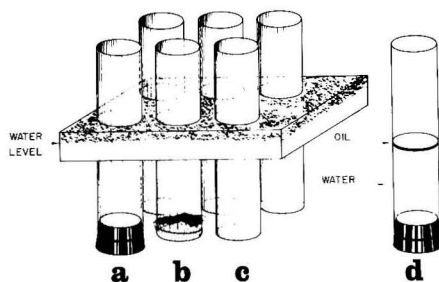


Figure 1. Diagram of apparatus employed for petroleum degradation tests in flow-through seawater tanks. For explanation see text

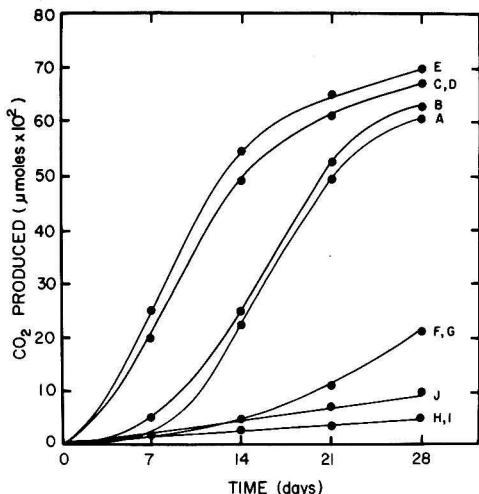


Figure 2. Influence of various nitrogen and phosphorus additives on the microbial CO_2 -production from petroleum on seawater. Additives: (A) $\text{KNO}_3 + \text{Na}_2\text{HPO}_4$, (B) CRNF-fertilizer + Na_2HPO_4 , (C) $\text{KNO}_3 + \text{octylphosphate}$, (D) $\text{KNO}_3 + \text{isooctylphosphate}$, (E) CRNF-fertilizer + octylphosphate, (F) dodecylurea + Na_2HPO_4 , (G) dodecylurea + octylphosphate, (H) trimethylenetetraurea + Na_2HPO_4 , (I) trimethylene-tetraurea + octylphosphate, (J) hexamethylphosphoramide

Results

Evaluation of Oleophilic N and P Sources. No measurable mineralization (conversion to CO_2) of the added petroleum occurred within four weeks in seawater samples that did not receive sources of nitrogen and phosphorus, nor was CO_2 evolution observed in flasks that received N and P sources but no petroleum. In the presence of a suitable P source, the tested nitrogen compounds showed widely varying abilities to support oil mineralization (Figure 2). While the CRNF paraffinized urea fertilizer (B, E) gave as good or better results than nitrate (A, C, D), dodecylurea (F, G) proved to be inferior, and trimethylenetetraurea (H, I) supported only a small fraction of the oil mineralization elicited by nitrate and CRNF. In the presence of a suitable nitrogen source, octylphosphate (C, E) and isooctylphosphate (D) supported significantly more rapid oil mineralization than inorganic phosphate (A, B). Hexamethylphosphoramide (J) as a combined N and P source performed poorly.

The gas chromatographic measurement of residual petroleum at the conclusion of the experiment (Table I) con-

firmed the conclusions drawn from the CO_2 -evolution patterns. On the basis of this experiment, CRNF fertilizer with octylphosphate was chosen as the most promising nutrient combination to be tested in a fieldlike situation.

Simulated Field Test. This experiment was designed to answer two critical questions. Are nitrogen and phosphorus limiting factors in oil biodegradation when the oil slick is not enclosed in a laboratory flask with a limited volume but is floating on an essentially infinite amount of seawater, and, is an oleophilic nitrogen and phosphorus fertilizer able to benefit selectively the oil-degrading microorganisms under the above conditions?

During the 42-day period of the experiment (May 9–June 20), the temperature of the seawater rose linearly from 15° to 20°C . The biodegradation of unsupplemented oil slicks was very slow in the circulating seawater system (Figure 3, A and A') and amounted to only 10% oil biodegradation in 42 days. No difference was observed between the open (A) and the membrane-closed tubes (A'), indicating that no losses had occurred through sinking of oil droplets from the open tubes. When the oil slicks in the open tubes were treated with nitrate and phosphate salts, only a slight and temporary increase in oil biodegradation was observed (B). In contrast, the same treatment resulted in a large early increase in the membrane-closed tubes (B') followed by a rate that became similar to the unsupplemented tubes (A and A'). Apparently, the dialysis membrane delayed the loss of nitrate and phosphate salts from these tubes. The greatest increase in oil biodegradation occurred, however, in the CRNF- and octylphosphate-treated slicks (C and C'). There was no difference between the stimulation in the open (C) and membrane-closed (C') tubes, showing that the fertilizer adhered strongly to the oil and was not eluted by circulating seawater.

Algal Growth. This experiment was conducted to test whether or not the application of a hydrophobic fertilizer triggers algal blooms. The chlorophyll concentration of unsupplemented seawater and of seawater treated with CRNF and octylphosphate was less than $0.0033 \mu\text{g/ml}$, the limit of detection for the procedure employed. In contrast, chlorophyll rose to $0.15 \mu\text{g/ml}$ in the flasks that were supplemented with nitrate and phosphate.

Discussion

Studies on an ecological problem, such as oil pollution, require that the natural situation be modeled as closely as possible. Laboratory tests are useful because they allow for controlled conditions, but they often radically alter the natural situation. Field experiments are often very difficult to conduct in a manner that is sufficiently controlled and quantitative to yield scientifically acceptable evi-

Table 1. Ability of Various Nitrogen and Phosphorus Sources to Support Oil Biodegradation

Nitrogen source	Phosphorus source	Oil biodegraded, %
KNO_3	Na_2HPO_4	70
KNO_3	Octylphosphate	72
KNO_3	Isooctylphosphate	70
CRNF	Na_2HPO_4	70
CRNF	Octylphosphate	72
Dodecylurea	Na_2HPO_4	37
Dodecylurea	Octylphosphate	35
Trimethylenetetraurea	Na_2HPO_4	15
Trimethylenetetraurea	Octylphosphate	15
Hexamethylphosphoramide	Hexamethylphosphoramide	15
None added	None added	5

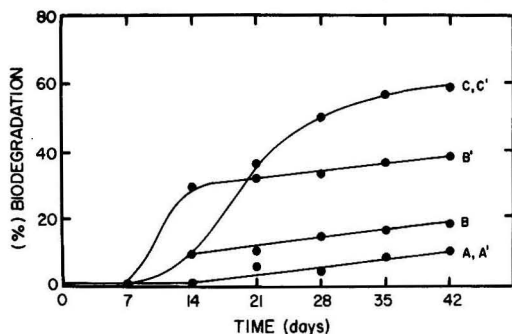


Figure 3. Influence of various nitrogen and phosphorus additives on oil biodegradation in flow-through seawater tanks. Symbols with prime indicate membrane-closed sample tubes. Symbols without prime indicate open tubes. Additives: (A, A') none, (B, B') $\text{KNO}_3 + \text{Na}_2\text{HPO}_4$, (C, C') CRNF-fertilizer + octylphosphate

dence. In some cases, floating frames were used in field experiments to contain an oil slick (*Chem. Eng. News*, 1970) but wind or current in excess of only a few knots renders the most elaborate floating barriers ineffective (Swift et al., 1969). Oil that escapes from the containment may be mistakenly considered as "degraded." Some workers have used stagnant seawater tanks of various sizes (Gunkel, 1967; Kator et al., 1971) but this experimental design limits the amount of available seawater. Quantitative and representative sample removal for analysis in the systems described above is very difficult (Kator et al., 1971). We believe that our experimental design with flow-through seawater and individual sample tubes solves some of these difficulties and may prove useful in future studies of similar nature.

Stimulated oil biodegradation as compared to other methods of oil cleanup has several desirable features but also some limitations. On the positive side, biodegradation is a natural process and, therefore, can be expected to have few undesirable ecological side effects. Biodegradation is not hampered by wind or wave action, it is expected to be relatively inexpensive, and can be carried out without elaborate machinery. On the other hand, its rate is inherently slower than that of physical removal or dispersion by detergents, and this rate may be further slowed by low water temperatures or by exhaustion of dissolved oxygen. Stimulated biodegradation has its proper role in an integrated oil pollution program, being applicable primarily to that portion of the spilled oil that escapes containment and spreads out too thinly to be collected by physical methods.

Most of the current effort directed toward the artificial stimulation of oil biodegradation (*Chem. Eng. News*, 1970) seems to be directed toward the development of proper bacterial inocula. However, it is important to remember that even the best inocula will fail in a nutritionally unfavorable environment. We suggest that such inocula should be combined with the type of fertilizers we described. Additionally, some marine environments seem to have sufficient indigenous microbial population to carry out extensive oil biodegradation if properly fertilized (Atlas and Bartha, 1973).

The CRNF fertilizer was shown here to be as good a source of nitrogen for oil-degrading microorganisms as KNO_3 , and octylphosphate was actually superior to Na_2HPO_4 . The latter may be explained with the fact that phosphate tends to precipitate in seawater while octylphosphate and isooctylphosphate remain available to the oil degraders. In addition, the surface active properties of octylphosphate may increase the oil surface available for microbial attack. CRNF and octylphosphate contribute relatively little to the BOD (N in CRNF = 26.8%; P in octylphosphate = 14.8%) and in preliminary tests this fertilizer combination failed to trigger algal blooms. Roughly, CRNF and octylphosphate will support the biodegradation of oil that is 10 and 100 times their own weights, respectively. The cost of such nutrient additives to treat 1 ton of spilled oil is estimated to be under \$15 (estimate based on manufacturers' recommended prices for CRNF and octylphosphate).

We do not claim that the described fertilizer formulation is necessarily the most effective and the most inexpensive, and practical use of the presented principle will require further commercial development, toxicity studies, and large-scale field trials. These matters are beyond our mission and facilities, and will best be handled by experienced commercial organizations. Our aim here has been to document the scientific validity of an idea—i.e., that oleophilic fertilizers are able to promote oil biodegradation on the high seas to a degree that invites practical exploitation.

Acknowledgment

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Determination of Alkylbenzenesulfonate (ABS) in Bottom Sediment

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■ A new method for the analysis of alkylbenzenesulfonate (ABS) in bottom sediments of a polluted river, a lake, and the sea was examined and the availability of the method was verified. Methylene blue active substance (MBAS) was extracted from dried mud sample with methanol-benzene (1:1) mixture. After the solvent was completely evaporated, the residue was dissolved into distilled water and the concentration of MBAS was determined according to a colorimetric method. The ratio ABS/MBAS in the MBAS was determined from the ratio of peak heights at wavenumber 1010 cm^{-1} and at 890 cm^{-1} of the infrared spectrum of MB-MBAS complex. Multiplying the value of MBAS by ABS/MBAS, the net content of ABS in the sediment was determined. Applying this method for the studies of polluted lake sediment and marine sediment, some geochemically interesting information on the process and rate of recent sedimentation in the lake and sea was obtained.

Alkylbenzenesulfonate (ABS), a main component of synthetic detergents, has been used for domestic and industrial purposes for more than 10 years in Japan. In Japan the amount of ABS consumed and discharged into the rivers and sewerage systems with waste waters during this period is estimated to be more than a million tons.

A part of ABS discharged into waterways in a soluble form or adsorbed on particulate matters in the water, is considered to be decomposed microbiologically, and the other part of the ABS finally goes to lakes or sea, where some of it will precipitate with particulate matter and accumulate in the bottom sediment.

The so-called hard type of ABS in synthetic detergents recently has been replaced by a more degradable soft type of ABS (LAS), and the concentration of ABS in natural waters has been somewhat reduced. The soft type of ABS, however, is also stable in the anaerobic condition in the bottom sediment of a polluted river or lake and will remain there for a long time.

Thus the bottom sediments of polluted water bodies are expected to contain ABS as a result of municipal pollution of water. An analytical method for determination of ABS in bottom sediment is examined in this paper.

While the concentration of ABS in river or lake waters is readily measurable (American Public Health Association, 1965) and there are many observation data, data on the measurement of the content of ABS in bottom sediment are lacking, supposedly because of the difficulty of the analysis of it in the mud and because ABS in the sediment has no apparent effect on our environment. The methylene blue colorimetric method, which is most commonly used for the analysis of ABS in water, cannot be used for sediment, because many kinds of interfering substances which form complex compounds with methylene blue are contained in the bottom mud. Though there are many modifications of the methylene blue colorimetric method (Longwell and Maniece, 1955; Abbot, 1962; Hill et al., 1962) to eliminate such methylene blue active substances (MBAS) other than ABS in the water, the con-

tents of such substances are so high in bottom mud that the application of these methods for the analysis of ABS in the sediments is difficult.

The separation of ABS from MBAS by thin layer chromatography was examined by Ōba (1965), but his method was too complicated and difficult to apply for a large number of samples of sediments.

The author recently developed a simple method to find the ratio of ABS to MBAS from the infrared spectrum of MB-MBAS complex (Ambe and Hanya, 1972). By application of that method to the analysis of ABS in bottom sediment, it became evident that the net content of ABS in the sediment could be easily determined.

Experimental

Samples. Bottom muds taken from the polluted river, a lake, and the sea by an Ekman-Birge-type grab and a plastic pipe core sampler were used as analytical samples.

Analytical Procedure. The combined method of methylene blue colorimetry and infrared spectrometry was applied to the aqueous solution of the extract from the mud sample. The concentration of MBAS was determined colorimetrically, and the ratio of ABS to MBAS (ABS/MBAS) was measured from the analysis of the infrared spectrum of the MB-MBAS complex. Multiplying the value of MBAS by ABS/MBAS, the content of net ABS in the sediment was obtained.

Extraction of MBAS. A wet sample of mud was centrifuged (3000 rpm, 30 min), and, after the supernatant water (interstitial water of the mud) was separated for the analysis of MBAS in it, the precipitated mud was dried at room temperature. The dried mud sample was ground and sifted with a sieve of 0.25 mm mesh. Ten grams of the dried sample mud was placed in a flask on a water bath (80°C) and refluxed with 100 ml of methanol-benzene (1:1) solution for 1 hr. The extraction was repeated three times with fresh solvent under the same conditions. All of the solvent used for these three extractions was mixed up and completely evaporated in a beaker on the water bath. The residue containing ABS was dissolved with about 50 ml of hot distilled water, removed to a volumetric flask, and made up to 100 ml with distilled water.

Determination of MBAS. Ten milliliters of the above solution was placed in a separatory funnel, and 0.5 ml of 0.1N H_2SO_4 , 1 ml of 0.015% methylene blue aqueous solution, and 10 ml of 1,2-dichloroethane were added. The separatory funnel was shaken for 1 min with a shaker, and the complex formed between methylene blue (MB) and MBAS was extracted into a layer of 1,2-dichloroethane. After washing this organic solvent layer with 10 ml of aqueous solution containing 0.01N H_2SO_4 and 0.013% methylene blue, the blue-colored MB-MBAS complex solution was filtered through glass wool to exclude emulsified water in it.

The absorbance of the MB-MBAS complex solution was measured at 655 nm with a Hitachi EPU-2A-type spectrophotometer, and the concentration of MBAS in the sample was determined using DBS (dodecylbenzenesulfo-

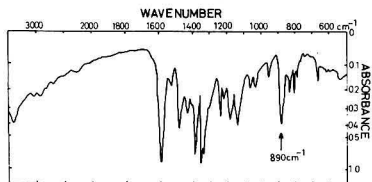


Figure 1. Infrared spectrum of methylene blue

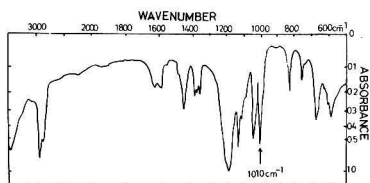


Figure 2. Infrared spectrum of ABS (dodecylbenzenesulfonate)

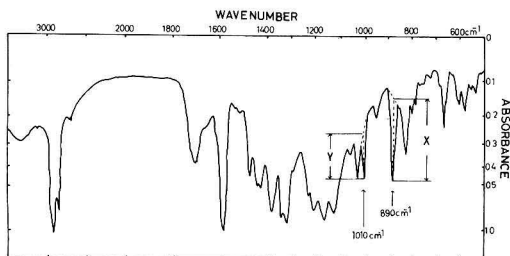


Figure 3. Infrared spectrum of MB-MBAS complex compound

The absorption peaks at wavenumber 1010 cm^{-1} and at 890 cm^{-1} are characteristic for ABS and MB, respectively

nate) as a standard. The results of the analysis of MBAS and ABS were represented as an equivalent mass of DBS.

Determination of ABS/MBAS. The solvent of the above solution of MB-MBAS complex was evaporated in a microcrucible, and about 3 mg of the residue was mixed thoroughly with 100 mg of potassium bromide to make a disk tablet for infrared spectrometry. The infrared spectrum was measured with a Hitachi EPI-G2 infrared spectrometer by potassium bromide disc method.

As shown in Figures 1, 2, and 3, the absorbance peaks of the infrared spectrum of the MB-MBAS complex at wavenumber 890 cm^{-1} and at 1010 cm^{-1} were characteristic for methylene blue and ABS, respectively. The ratio of the peak height at 1010 cm^{-1} , Y, to the peak height at 890 cm^{-1} , X (Figure 3), was proportional to the ratio of ABS to MB in the MB-MBAS complex compound. As 1 mole of ABS combines with 1 mole of methylene blue (Otsuki et al., 1964) and the concentration of MBAS is represented as DBS, the ratio of ABS to MB is equal to the ratio of ABS to MBAS.

$$\frac{Y}{X} = \alpha \times \frac{\text{ABS (mole)}}{\text{MB (mole)}} = \alpha \times \frac{\text{ABS (DBS equivalent mass)}}{\text{MBAS (DBS equivalent mass)}}$$

where α is a constant. The value of α was 0.78 in this experiment.

Table I. Recovery of Added ABS (DBS)

Sample (lake mud)	No. 1, $\mu\text{g/g}$	No. 2, $\mu\text{g/g}$
MBAS originally present	10	10
ABS originally present	0	0
Added ABS (DBS)	45	15
Total MBAS	55	25
Total ABS	45	15
Found MBAS	50	21
Found ABS (= recovered ABS)	43	14
Percent of recovery of ABS	95	93

By use of a calibration curve for relation between Y/X and ABS/MBAS constructed with a standard solution, the ratio ABS/MBAS of the MBAS in the sample was determined. Multiplying the MBAS concentration by ABS/MBAS gave the net content of ABS in the mud.

Results and Discussions

Extraction of MBAS. The extractability of MBAS from the mud sample cannot be exactly determined because the content of MBAS originally contained in the sample is unknown. However, as no more MBAS was extracted after the extraction was repeated three times with fresh solvent, almost all of the MBAS in the mud is considered to have been removed to the solvent. Furthermore, ABS adsorbed on the surface of the particles of the mud is thought to be readily extractable, and, as the content of ABS is calculated by multiplying MBAS by ABS/MBAS, it does not affect the final result of the analysis of ABS whether the extraction of MBAS other than ABS is complete, inasmuch as the extraction of ABS is complete.

According to the recovery test by the addition of DBS to lake muds, as shown in Table I, more than 93% of the added ABS was recovered and identified as ABS.

Determination of MBAS. As the limit of detection for the analysis of MBAS in water by this method is 0.03 mg/l (Ambe and Hanya, 1972), 0.3 $\mu\text{g/g}$ of MBAS in mud sample can be detected.

However, such a small amount of MBAS is insufficient to obtain a precise pattern of infrared spectrum which is available for the analysis of the absorbance peaks due to ABS and methylene blue.

In such a case, an extraction on a larger scale, using much more sample and solvent as described before, is necessary to get a sufficient amount of MBAS.

Calibration Curve for ABS/MBAS. A calibration curve for the relationship between Y/X and ABS/MBAS was constructed using standard samples of MBAS containing ABS in different ratios.

The standard MBAS samples were prepared by mixing the following two solutions in appropriate ratios so that the ratio ABS/MBAS had several values between 0 and 1:

Solution 1: 1,2-dichloroethane solution of MB-ABS complex prepared from a standard aqueous solution of DBS.

Solution 2: 1,2-dichloroethane solution of the complex of methylene blue and MBAS without ABS. This MBAS without ABS was prepared extracting from the bottom mud of an unpolluted lake (Lake Motosu, Japan).

The concentration of MBAS in each solution was determined by colorimetry and both solutions were adjusted to equal concentration by dilution.

The calibration curve gave a straight line which passed the origin and the point ABS/MBAS = 1 against Y/X = 0.78.

Table II. MBAS and ABS Found in Reproducibility Study

	Sample 1 (marine sediment)			Sample 2 (river sediment)		
	MBAS, μg/g	ABS/ MBAS	ABS, μg/g	MBAS, μg/g	ABS/ MBAS	ABS, μg/g
	33	0.33	11	55	0.32	18
	37	0.30	11	65	0.33	21
	35	0.27	9	65	0.28	18
	37	0.28	10	60	0.29	18
	34	0.27	9	—	—	—
Mean	35	0.29	10	61	0.31	19
Rel std dev	±4.3%	±7.2%	±10%	±6.7%	±6.8%	±7.0%

Absorption Peaks at 1010 cm^{-1} and 890 cm^{-1} . The chemical composition and property of MBAS other than ABS are not exactly known. However, as the MBAS extracted from several unpolluted sediment (for example; Lake Motosu, Lake Kizaki, Lake Aoki, Lake Shoji, and Sagami Bay) showed no infrared absorption peak at 1010 cm^{-1} , it is probable that the natural MBAS does not contain any interfering material which gives an infrared absorption peak at that wavenumber. The 890 cm^{-1} peak is specific for methylene blue, and, as the spectrum of MB-MBAS at that wavenumber showed no difference from the spectrum of the same quantity of pure methylene blue, it was concluded that no perturbation on the infrared spectrum of methylene blue at near that wavenumber occurred owing to the formation of complex with MBAS.

Since the absorption peak at wavenumber 1010 cm^{-1} is considered to represent sulfonate in the ABS molecule (American Public Health Association, 1965), both the hard type of ABS and soft type of ABS (LAS) are determined together by this method.

Reproducibility of Analysis. The amounts of MBAS and ABS found in the reproducibility test for river and marine sediments are shown in Table II. The relative standard deviation for the determination of the contents of MBAS, ABS/MBAS, and ABS in both of the two samples in this test was smaller than 7%, 8%, and 10%, respectively.

Thus we could determine the content of ABS in bottom sediment with relative standard error below $\pm 10\%$.

Applications

ABS in Sediment of Lake Suwa. Lake Suwa, situated in the central part of Japan, is one of the most polluted

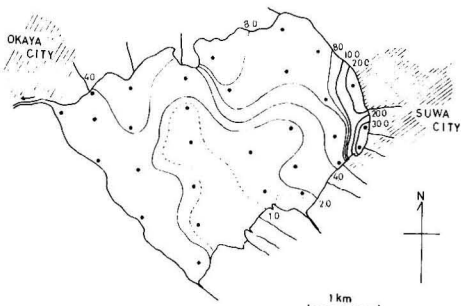


Figure 4. Distribution of ABS content in the surface of the bottom sediment of Lake Suwa, Japan ($\mu\text{g/g}$ of dry weight)

Dashed line is the contour of 1.0 $\mu\text{g/g}$ (August, 1971)

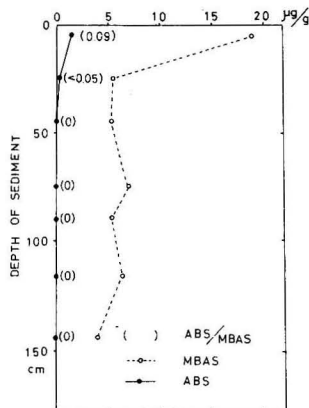


Figure 5. Vertical distribution of MBAS, ABS/MBAS, ABS in the bottom sediment at the point off Yokohama in the Tokyo Bay, Japan (December, 1969)

lakes in Japan. The diameter of the lake is 5 km, the maximum depth is only 7 meters and the water is highly polluted with waste water. Suwa City, with a population of about 70,000, and a part of another city (Okaya City) lie on the shore of the lake, discharging many kinds of waste water into the lake.

The amount of ABS flowing into the lake is estimated to be about 70 tons/year, and a considerable part of it is expected to have deposited in the bottom of the lake.

The contents of MBAS and ABS in the surface of the lake sediment were measured according to the above method. The distribution of ABS in the sediment is shown in Figure 4. The content of MBAS in the lake mud was higher in the northern part of the lake, but in the south it was lower. The value of ABS/MBAS ranged from nearly zero to about 0.5, and the higher value appeared also in the region along Suwa City. Accordingly, ABS was higher in the northeastern part of the lake, especially in the region near Suwa City, where very high values (20–30 $\mu\text{g/g}$) were found reflecting the pollution by the inflowing urban waste waters. Thus, the ABS adsorbed on the suspended matters in the polluted river waters flowing into the lake is considered to have deposited immediately after the mixing with stagnant lake water.

Vertical Distribution of ABS in Marine Sediment. A vertical distribution of the content of ABS in the marine sediment was measured for a core sample taken from the bottom of Tokyo Bay. The result is shown in Figure 5.

A core sample was taken with a plastic pipe core sampler by a skin diver, at the point about 5 km off the coast of Yokohama Harbor with the depth of water 20 meters (December 1969).

The water of Tokyo Bay is highly polluted with domestic and industrial waste water and amounts of ABS are observed to flow into the bay from several polluted rivers, and some of it is expected to have deposited on the bottom of the bay.

The sample of the bottom sediment was composed of black mud with a smell of hydrogen sulfide, reflecting an anaerobic condition in the bottom. As shown in Figure 5, ABS was found only in the uppermost 30-cm thick layer in the sediment, and no ABS existed in the sediment below it. Considering that the decomposition of ABS is very low under the anaerobic conditions in the sediment, it is probable that the ABS-containing layer has deposited since the inflow of ABS from the waste waters began. If

we can assume that no perturbation in the stratification of the sediment and no permeation of water containing ABS into the sediment have occurred since the beginning of the deposition of ABS, the average rate of sedimentation can be calculated from the thickness of ABS-containing layer and the number of years of ABS use.

The date of the beginning of the deposition of ABS in Tokyo Bay was estimated to be about 10 years before the time of sampling of the sediment, according to the data on the production of synthetic detergents in Japan and the secular change of ABS in the water of the River Tama, one of the main polluted rivers flowing into Tokyo Bay.

The average rate of sedimentation was calculated as 3 cm/year in this point, and one of the examples of the usefulness of ABS as a geological tracer was presented. Though the time range in which ABS can be used is limited to only 10–20 years, such an estimation by a man-made substance is promising to apply in the area where the sedimentation process is very rapid, as in an estuary.

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Permeation of Sulfur Dioxide Through Polymeric Stack Sampling Interfaces

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■ Preliminary developmental studies on the use of a cylindrical polymeric tube as a permeable interface between a stack and a continuous ambient SO₂ monitor have been carried out under controlled laboratory conditions. Isothermal SO₂ trans-wall flux measurements were made over a range of concentrations of SO₂ in air at several temperatures, using PTFE Teflon, silicone rubber, and fluorosilicone rubber tubes. The flux varied linearly with the trans-wall concentration gradient in all cases. The activation energies in kcal/g-mol for permeation of SO₂ were 7.0 for Teflon, 0.94 for the silicone rubber, and 1.33 for the fluorosilicone rubber. The relaxation times, or times required for the fluxes to reach steady-state values following changes in operating conditions, were on the order of minutes for each material. The results of these preliminary studies indicate that the polymer tube interface is a promising device for stack monitoring.

Stack-gas monitoring on a continuous basis has become important in many industrial processes. The Clean Air Act of 1970 specifies that air pollution control implementation plans must include emission standards and requirements for monitoring stationary source emissions. If individual sources are to meet these standards, control equipment will have to be installed; because of the added operating expense of this equipment, optimal performance of this equipment may be essential. A continuous stack

monitor can measure and record the efficiency of control devices, and under some circumstances can be integrated into a process control system to monitor product and by-product losses.

A number of factors, such as high particulate loadings, high temperatures, and high humidities, can complicate the process of obtaining and analyzing a representative gas sample from a stack. To minimize the effects of these conditions, an interface between the stack and the gas analyzer must be devised to condition the sampled gas. Research programs on pollutant analyzer systems, especially for ambient SO₂ monitoring, have resulted in the development of several commercially available analyzers (see, for example, Stevens et al., 1971); incorporating these analyzers into the sampling system with an interface device is a logical step toward continuous stack monitoring.

Stack sampling interface systems have been described by Nacovsky (1967), Thoenes and Guse (1968), Risk and Murray (1964), Rossano and Cooper (1968), and many others. These systems are adequate for short-term applications, but require continuous surveillance when used for longer periods of continuous sampling. Some of the maintenance problems include rapid clogging of particulate filters, fluctuations in gas flow aggravated by multiple streams, flowmeter malfunctions, and malfunctions in the continuous analyzer caused by minute quantities of particulates or an excessive pressure-flow fluctuation in the sample line.

The use of a polymeric barrier as a sampling interface between the stack and the analytical system has been proposed to alleviate these problems (O'Keeffe, 1970). The polymeric material might be in a tubular form such that a

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carrier gas could be passed through the inside of the tube, while the outside tube surface would be exposed to the stack. The resulting pollutant concentration gradient would then lead to permeation of the pollutant through the tube wall into the carrier gas. The advantages of this approach are that a high dilution factor could be obtained with only a moderate carrier-gas flow rate; the use of a dry carrier gas should result in a very low dew point, even if some water vapor diffused through the tube wall; particulate buildup of the type characteristic of ordinary flow-through filtration would be eliminated since transport of the pollutant would be entirely diffusive, and the proper arrangement of the polymer tube could automatically provide a response proportional to the area-averaged pollutant concentration in the stack.

With these considerations in mind a developmental program on the use of polymeric interfaces for the stack sampling of SO₂ has been undertaken. Several phases of this program will be devoted to the determination of the effects of particulate deposition and water vapor permeation on the device performance and the operating characteristics of the device under actual process stack conditions. The first phase of the program, reported in this paper, concerns the measurement of SO₂ permeabilities of tubular sampling devices under controlled laboratory conditions. The specific objectives of the study were to find a polymeric material permeable to SO₂ which could withstand typical stack temperatures and would be likely to resist particulate deposition and water permeation, to observe whether measurable fluxes of SO₂ through the tube wall could be achieved for typical stack concentrations, to determine how easily these fluxes could be correlated with the stack concentrations, and to measure the time required for the system to respond to changes in the stack concentration. To exclude interfering effects, the simulated stack gas consisted only of SO₂ in air.

Experimental

A schematic diagram of the experimental system is shown in Figure 1. All lines and fittings except those otherwise identified were stainless steel.

To expose the outside surface of a measured length of polymer tubing to simulated stack temperatures and SO₂ concentrations, a glass chamber was constructed by clamping 6-in. square stainless steel end plates with Teflon gaskets to the ends of a 3-in. i.d. Pyrex glass pipe 24 in. long. The end plates were drilled and tapped to accept a thermocouple bulkhead fitting, a 0.125-in. tube fitting, and a 0.375-in. tube fitting in each plate. The 0.375-in. fittings were drilled internally to allow a length of 0.375-in. tubing to pass through the end plates to fittings inside the chamber. A 1/8-in. diameter stainless steel support rod was inserted inside the polymer tube to be tested and the tube was connected at either end to the internal fittings. The chamber assembly was then placed inside a thermostatically controlled oven, adjustable to a maximum temperature of 250°C.

A mixture of 5200 ppm SO₂ in air and a dilution stream containing less than 0.1 ppm SO₂ in air were fed from cylinders through rotameters and into a tee to make up the simulated stack gas. The combined stream passed through an access port on the oven, a 0.125-in. chamber end plate fitting, the chamber on the outside of the polymer tube, the opposite 0.125-in. fitting, and out of the oven to a hood.

The carrier gas into which the SO₂ permeated consisted of room air pumped through an activated charcoal scrubber and a rotameter by a carbon vane pump. The purified air entered the oven and passed through a 0.375-in. fit-

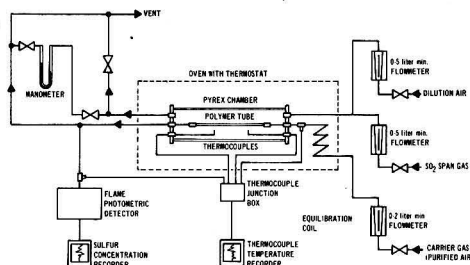


Figure 1. Diagram of apparatus

ting, the inside of the polymer tube, the opposite 0.375-in. fitting, and out of the oven to a flame photometric detector, which measured the total sulfur concentration in the stream. A 7-in. strip chart recorder permitted continuous monitoring of the detector signal.

Two thermocouples passed through the 0.125-in. chamber end plate fittings, and measured the temperature at two points near the outside surface of the polymer tube. The temperature of the carrier gas stream was monitored at the inlet and at the inlet of the photometric detector. A manometer measured any pressure difference that might exist between the gases on the inside and outside of the polymer tube.

The flame photometric detector was calibrated using gravimetrically calibrated permeation tubes, as described by Stevens et al. (1969). A log-linear amplifier permitted measurements by the detector to the nearest 0.005 ppm in the most sensitive range (<0.20 ppm), but difficulties in setting the sample flow on the analyzer limited the precision to an estimated ± 0.01 ppm. Continuous measurement of the oven temperature indicated that the thermostat could maintain the temperature within $\pm 1^\circ\text{C}$ of a desired value.

The procedure for measuring SO₂ flux values for a polymer tube was as follows. The polymer tube was connected to the fittings in the chamber, and the exposed length of the polymer surface was measured. The chamber was sealed and purged with the required SO₂-air mixture. The oven thermostat was set and the surface temperature of the polymer was monitored until it reached the desired temperature. The manometer was checked and the pressures of the carrier gas stream and the purge gas were equalized, if necessary. The carrier gas flow rate was set at 1.0 l./min and the sample flow on the flame photometric detector was set at 200 cc/min. When the recorder trace indicated that the diffusion of SO₂ through the polymer tube wall into the carrier gas stream had reached steady state, the SO₂ concentration (in ppm) indicated by the detector was noted and corrected for background SO₂ in the carrier gas. The background concentration averaged approximately 0.025 ppm SO₂. The flux of SO₂ through the tube wall was calculated from the corrected concentration of SO₂ in the carrier gas, the carrier gas flow rate, and the length of the exposed tube surface.

After a step increase in the chamber gas concentration was imposed at a given temperature, the time required for the detector to sense a change in the carrier gas-SO₂ concentration was noted and designated as the breakthrough time. The total time from the initiation of the step change until an approximate steady-state trace on the recorder was achieved was designated the relaxation time.

SO₂ fluxes were measured over a range of temperatures from 93.3–232°C for simulated stack concentrations from 950–5200 parts per million (by volume) SO₂ in air, using

tubes made of three polymeric materials: polytetrafluoroethylene (PTFE Teflon), a silicone rubber, and a fluorosilicone rubber. The latter two polymers are manufactured by the Dow Corning Corp., and are designated as SILASTIC 437 base and SILASTIC LS-63U, respectively.

Permeation Formulas

The solution of the equation for steady-state diffusion of a gas into a hollow cylinder with a constant diffusivity is given by Crank and Park (1968) as

$$F = \frac{2\pi D(C_2 - C_1)}{\ln(b/a)} \quad (1)$$

where

F = diffusive flux into the tube, cm^3 (STP)/sec-cm (length)

D = diffusivity, cm^2/sec

C_1, C_2 = concentrations of dissolved gas at the inner and outer tube surfaces, respectively, cm^3 (STP)/ cm^3 (polymer)

a, b = inner and outer tube radii, respectively, cm

It is convenient to express the flux in terms of the bulk-phase partial pressures of the permeating gas. From Henry's law

$$C = Sp \quad (2)$$

where

p = partial pressure, cm (Hg)

S = solubility, cm^3 (STP)/ cm^3 (polymer)-cm (Hg)

and C is again the dissolved gas concentration. Equation 2 for C is substituted into Equation 1, and the result is expressed in terms of the permeability

$$P \left[\frac{\text{cm}^3 \text{ (STP)} - \text{cm}^2}{\text{sec} - \text{cm}^3 \text{ (polymer)} - \text{cm} \text{ (Hg)}} \right] = DS \quad (3)$$

to yield
$$F = \frac{2\pi P(p_2 - p_1)}{\ln(b/a)} \quad (4)$$

The principal assumptions leading to Equation 4—a constant diffusivity and the applicability of Henry's law—have their greatest validity for the permeation of gases at constant temperature and low partial pressures (Stannett, 1968), the conditions of the present experiments.

The temperature dependence of the permeability is expected to follow an Arrhenius relationship over moderate temperature ranges (Stannett, 1968):

$$P = P_o \exp(-E_p/RT) \quad (5)$$

where E_p is the activation energy for permeation. If the solubility, S , is not highly dependent on temperature, E_p is approximately equal to the activation energy for diffusion E_d .

It is possible to obtain values for both the diffusivity, D , and solubility S from the permeability and the relaxation time, using the "time-lag" method (Crank and Park, 1968). These values were not required for the purposes of this study, however, and so the calculations were not performed.

Data Reduction and Results

The partial pressure of SO_2 on the outside of the tube, p_2 , was always at least two orders of magnitude greater than that in the carrier gas, p_1 , so that if the assumptions which underlie Equation 4 are valid, a plot of the measured flux F vs. $2\pi p_2/\ln(b/a)$ for a specific tube material and temperature should be a straight line, with slope P . Such plots are shown in Figures 2-4. The linearity of these plots and the coincidence of the points obtained for

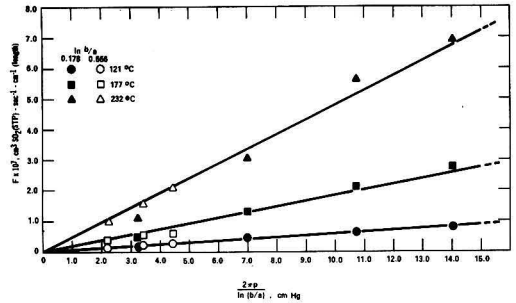


Figure 2. Flux vs. SO_2 partial pressure, PTFE Teflon tubes

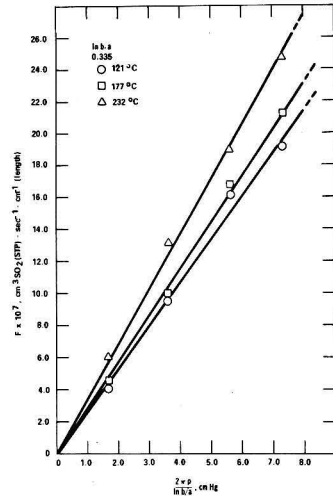


Figure 3. Flux vs. SO_2 partial pressure, silicone rubber tube

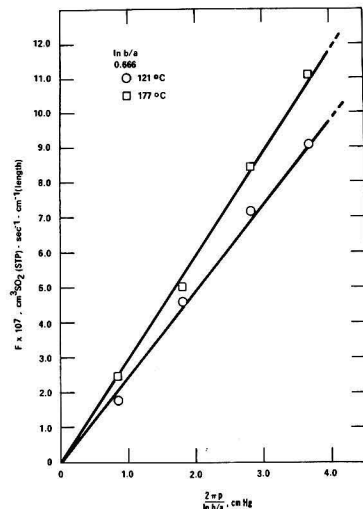


Figure 4. Flux vs. SO_2 partial pressure, fluorosilicone rubber tube

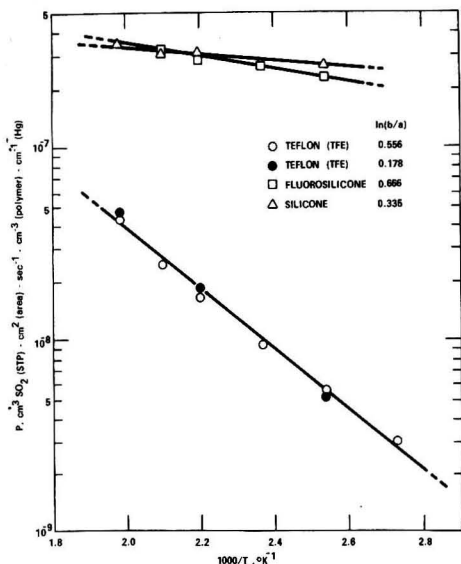


Figure 5. Log permeability vs. inverse temperature

PTFE Teflon using two different tube wall thicknesses confirm the validity of Equation 4 for the conditions of the experiment.

Table I lists the permeabilities obtained by applying linear regression to the data of Figures 2-4. The correlation coefficients were greater than 0.99 in all cases.

From Equation 5, an Arrhenius plot of $\ln P$ vs. $1/T$ for a specific tube material should yield a line with slope equal to the activation energy for permeation divided by the gas constant. Such plots and the corresponding least-squares lines are shown in Figure 5 for the three materials tested. The resulting activation energies and standard deviations are listed in Table II.

The sensitivity of the measured permeabilities to tem-

Table I. SO₂ Permeabilities

Tube material	T, °C	$p^a \times 10^8$	$\sigma^b \times 10^8$
PTFE Teflon ^c	93.3	0.299	0.044
	121.0	0.576	0.049
	149.0	0.923	0.049
	177.0	1.54	0.16
	204.0	2.34	0.06
PTFE Teflon ^d	232.0	4.27	0.54
	121	0.539	0.140
	177	1.81	0.16
Silicone rubber ^e	232	4.48	0.84
	121	26.2	2.1
	177	28.1	1.7
Fluorosilicone rubber ^f	204	31.3	1.3
	232	34.8	1.3
	121	23.6	2.2
Fluorosilicone rubber ^f	149	25.8	1.9
	177	28.8	1.5
	204	31.6	1.5

^a Permeability, $\text{cm}^3 \text{SO}_2 \text{ (STP)} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1} \cdot \text{cm}^{-3}$ (copolymer) $\cdot \text{cm}^{-1}$ (Hg).

^b Standard deviation in P.

^c PTFE Teflon tube, 0.478 cm i.d. \times 0.834 cm o.d.

^d PTFE Teflon tube, 0.788 cm i.d. \times 0.940 cm o.d.

^e Silicone tube, 0.598 cm i.d. \times 0.835 cm o.d.

^f Fluorosilicone tube, 0.325 cm i.d. \times 0.650 cm o.d.

Table II. Activation Energies for SO₂ Permeation

Material	E_p , kcal/g-mol ^a
PTFE Teflon	6.99 ± 0.51
Silicone rubber	0.94 ± 0.80
Fluorosilicone rubber	1.33 ± 0.35

^a Given error bounds are the 95% confidence limits.

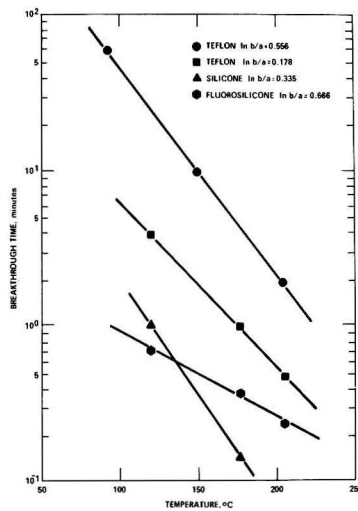


Figure 6. Breakthrough times vs. temperature

perature fluctuations can be estimated from these activation energies. At 121°C, for instance, a 2°C rise in T increases P by 4.7% for Teflon, 0.6% for the silicone rubber, and 0.9% for the fluorosilicone rubber.

Breakthrough and relaxation times were measured by allowing each tube to equilibrate at a fixed temperature with no SO₂ in the chamber, then purging the chamber with approximately five chamber volumes of air containing a known concentration of SO₂ over a period of 3-4 min and monitoring the response. Figures 6 and 7 show the breakthrough and relaxation times obtained at various temperatures for the four tubes tested.

Discussion and Conclusions

Four principal parameters must be specified in designing a device of the type in question: the material of construction, the tube wall thickness, the tube length, and the carrier gas flow rate. The ultimate objective of developmental studies of the type presently under way is to be able to specify values of these parameters for any given stack conditions.

The tube must have a permeability which is neither too low nor too high, so that the pollutant concentration in the gas to be analyzed is within the detection range of the analyzer, and the permeability must remain constant for relatively long periods of time at the stack operating conditions. The temperature response of the tube should be predictable, so that compensation for fluctuations in the stack temperature can be made in analyzing the response data. Particularly if large temperature fluctuations are expected, a low activation energy for permeation is desirable to minimize the effect of the fluctuations on the response. The response time of the device is also critical: If the re-

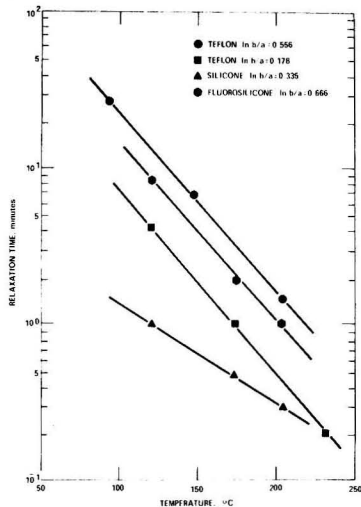


Figure 7. Relaxation times vs. temperature

sponse is too slow, the device would not be suitable for process control applications, while if it is too fast, it could yield erratic traces which would be difficult to average. Finally, the tube chosen would have to maintain its performance characteristics under the existing stack humidity and particulate loading conditions.

Of the three tube materials tested in this preliminary study, the fluorosilicone rubber and the PTFE Teflon appear suited to operation in stacks at temperatures up to about 230°C; the silicone rubber appeared to undergo embrittlement after 72 hr at 232°C. All of the tubes tested provided SO₂ concentrations in the range 0.1–1.0 ppm, suitable for analysis by ambient gas monitors, for simulated stack SO₂ concentrations in the range 950–5200 ppm.

The recently proposed Environmental Protection Agency standards for new stationary sources require 2-hr averages to show compliance; this suggests that a permeation tube with a relaxation time of, say, 5 min or less would be more than satisfactory from this point of view. The data of Figure 7 indicate that the silicone rubber tube would be adequate above about 150°C, and the thin-walled Teflon tube above about 200°C.

Since the relaxation time correlates well with the logarithm of the ratio of the outer to the inner tube radius, the

wall thickness needed to provide any desired relaxation time can be calculated with relative ease. After the radial dimensions of the tube have been determined to provide the desired relaxation time, the length of the tube and the carrier gas flow rate could be chosen to provide a concentration of SO₂ in the carrier gas within the range of the available gas analyzer, using an estimated stack SO₂ concentration, an experimentally determined or tabulated permeability, Equation 4 for the trans-wall SO₂ flux F , and the relationship

$$C_a = FL / \phi \quad (6)$$

where C_a is the SO₂ concentration in the analyzed gas, L is the tube length, and ϕ is the carrier gas volumetric flow rate.

Work is currently under way to determine the effects of particulates and moisture on the performance of the device, to establish the performance characteristics of prototype devices under power plant and industrial process stack conditions, to screen a wide variety of single and composite tube materials, and to extend the studies to pollutants other than SO₂. The final word on the feasibility of the device must of course await the completion of these studies; however, the predictability of the fluxes and the low relaxation times achieved in the preliminary studies provide considerable encouragement.

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Chemiluminescent Reactions of Peroxyacetyl Nitrate and Ozone with Triethylamine

Possible Atmospheric Monitor for Peroxyacetyl Nitrate

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■ Chemiluminescence spectra from the gas phase reactions of peroxyacetyl nitrate (PAN) ($\lambda_{\text{max}} \sim 650 \text{ nm}$) and ozone ($\lambda_{\text{max}} \sim 520 \text{ nm}$) with triethylamine have been obtained at atmospheric pressure. The two chemiluminescent reactions are easily distinguishable by optical filters. Concentrations of PAN as low as 6 ppb were detected by this chemiluminescence technique. The application of this method as an atmospheric monitor for PAN is discussed.

Very sensitive chemiluminescence techniques have been developed recently to monitor atmospheric concentrations of ozone and nitric oxide. Three different chemiluminescent techniques have been employed for the measurement of ozone. Regner's (1960, 1964) method utilizes the luminescence emission produced from the reaction of ozone with rhodamine-B adsorbed on activated silica gel. A more convenient technique for the continuous air pollution monitoring of ozone is based upon the chemiluminescence produced in the reaction between ozone and ethylene at atmospheric pressure (Nederbragt, et al., 1965; Warren and Babcock, 1970).

The low-pressure chemiluminescent reaction between nitric oxide and ozone, developed by Fontijn et al. (1970), can be used to monitor either atmospheric ozone or nitric oxide. This technique has recently been expanded by Hodgeson et al. (1971) for the measurement of total oxides of nitrogen or, with modifications, NO_x plus ammonia. Furthermore, it has been suggested by Kummer et al. (1971) that it may be feasible to determine quantitatively trace amounts of sulfur-containing pollutants by means of their chemiluminescent reactions with ozone.

Peroxyacetyl nitrate (PAN) is one of the key oxidants formed in photochemical smog. Ambient concentrations of PAN as high as 30 ppb are not uncommon in the eastern end of the Los Angeles basin (Darley et al., 1963). PAN is a known eye irritant (Stephens et al., 1961) and phytotoxicant; thus it has been pointed out by Taylor (1969) that acute injury occurs to sensitive plants after 4 hr of exposure to approximately 14 ppb PAN in ambient air. The most serious PAN episode reported to date occurred in Riverside in 1972 in which daily maximum PAN readings exceeding 15 ppb were recorded for 23 days (readings exceeded 40 ppb on two consecutive days) during the month of March. PAN is currently monitored in the atmosphere by gas chromatography on a repetitive batch basis (Stephens and Price, 1973). Presently, no chemiluminescence technique exists for atmospheric monitoring of PAN (Fontijn, 1972). A versatile chemiluminescence-monitoring technique would permit continuous determination of atmospheric levels of PAN.

Initial chemiluminescence studies with PAN and amines demonstrated that tertiary amines, when reacted

with PAN, produced chemiluminescence. We now report the characteristic chemiluminescence spectra produced from the gas phase reactions of peroxyacetyl nitrate (PAN) and ozone with triethylamine vapor. Concentrations of PAN as low as 6 ppb were detectable with our current apparatus; consequently, emphasis will be placed on utilizing the chemiluminescence as a possible atmospheric monitor for PAN.

Experimental

The reaction vessel consisted of a silvered 1-liter chemiluminescence cuvette provided with two gas inlets centered above the optical window which formed the bottom of the cuvette. Light generated in the reaction cuvette was chopped mechanically at 330 Hz and the output of the multiplier phototube (E.M.I. 9659 QD) was fed into a lock-in amplifier (Princeton Applied Research, Model HR8). Cutoff filters were mounted in a wheel arrangement

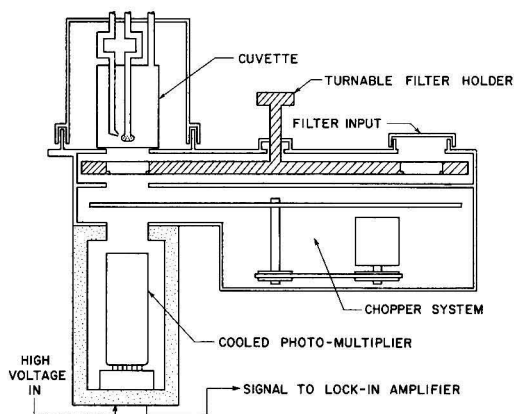


Figure 1. Chemiluminescence detection unit

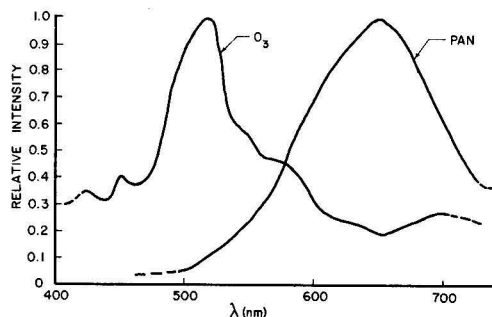


Figure 2. Emission spectra of chemiluminescence reactions of triethylamine with PAN and ozone. Relative intensity maximum arbitrarily set at unity

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between the optical window and mechanical chopper (Figure 1). Low-resolution spectra were obtained with a Bausch and Lomb monochromator (Model 33-86-03) located between the chopper and multiplier phototube. The amplified signals were displayed on a 100-mV potentiometric Sargent recorder (Model SRG). The monochromator-multiplier phototube unit was calibrated by use of a standard lamp (G.E. quartz iodine lamp EPI-1452, 1000 W) and the spectra were corrected for spectral sensitivity.

Identical spectra were obtained whether the amine was added to the reaction cuvette in a stream of nitrogen or whether an excess of amine (liquid-vapor equilibrium) was present in the cuvette. Variable concentrations of both PAN and ozone were prepared and passed into the cuvette at a constant flow rate (~ 10 cc/sec). All experiments were performed at room temperature.

Peroxyacetyl nitrate (1000 ppm, pressurized tanks) was kindly provided by the University of California Statewide Air Pollution Research Center at Riverside. Ozone ($\sim 2\%$ V/V) was produced by passing oxygen (Matheson, ultra-high-purity grade) through a Welsbach Model T-408 ozonizer. Triethylamine (Matheson, Coleman & Bell or Mallinckrodt gave identical results) was checked for purity by glc ($>99.95\%$) and used without further purification.

Results and Discussion

Corrected low-resolution spectra of the light emissions produced in the reactions of PAN (1000 ppm) and ozone (20,000 ppm) with triethylamine vapor were obtained independently and are shown in Figure 2 for comparison. The relative intensity maximum was arbitrarily set at unity. The maxima were separated by approximately 130 nm.

In control experiments, methyl nitrate, ethyl nitrate, ethyl nitrite, and NO_2 , all of which are possible contaminants of PAN, were mixed with triethylamine vapor in the reaction cuvette and showed no evidence of luminescence. In a similar control experiment, the reaction of nitric oxide (1000 ppm) with triethylamine resulted in a weak luminescence which was enhanced in the presence of air. However, the emission observed from 10 ppm nitric oxide was insignificant compared to that produced from 0.4 ppm PAN.

Concentrations of PAN as low as 6 ppb were detected with our current apparatus. This is nearly as sensitive as present gas chromatographic techniques (Smith et al., 1971). Improvement of the light detection system may permit measurement of PAN concentrations as low as 1 ppb or less.

The reaction of PAN with triethylamine produced a slowly decaying afterglow which lasted for several minutes even at the lowest PAN concentrations employed. This behavior is contrasted to that of the corresponding ozone reaction in which the emission rapidly decayed after the ozone flow ceased. The respective decay curves are illustrated in Figure 3.

To distinguish the chemiluminescence induced by the reaction of triethylamine with concentrations of PAN and ozone found in polluted urban atmospheres, various combinations of cutoff filters were tested. A 500-nm cutoff filter (transparent: $\lambda < 550$ nm) in conjunction with a 665-nm cutoff filter (transparent: $\lambda > 665$ nm) provided relative intensity values characteristic for both the PAN and ozone induced emissions. In the case of ozone-triethylamine reaction, a value of $I_{665}/I_{500} < 1$ was predicted from the monochromator spectra shown in Figure 2; for the PAN-triethylamine reaction, a value of $I_{665}/I_{500} > 1$ was predicted. The measured values of I_{665}/I_{500} were 0.35 and 3.44 for the ozone-amine and the PAN-amine reactions,

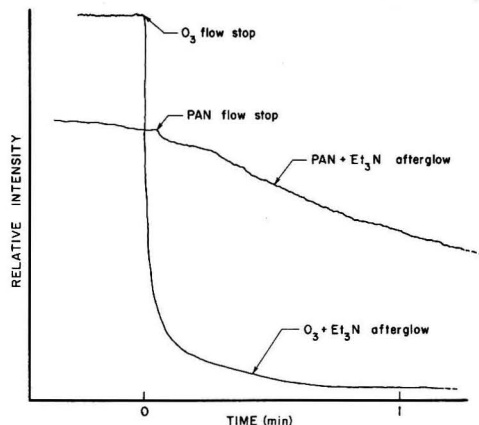


Figure 3. Decay curves of chemiluminescence generated in reaction of triethylamine with PAN and ozone

respectively. This combination of cutoff filters affords the most appropriate means of distinguishing the two emissions at low concentrations of PAN and O_3 where the use of a monochromator is not feasible.

To test the cutoff filter technique, the chemiluminescence produced by a mixture containing a 20-fold excess of ozone to PAN, a ratio not uncommon in polluted ambient air, was investigated. In this particular case, a value of I_{665}/I_{500} of 1.35 was found, indicating a much greater chemiluminescence efficiency for the PAN-amine reaction in contrast to the ozone-amine reaction.

In an experiment designed to measure the chemiluminescence efficiency of the PAN-amine reaction relative to the corresponding O_3 -amine reaction, 1.5 ppm of O_3 produced the same uncorrected overall integrated light intensity as 0.4 ppm PAN in reaction with the amine. As an approximate correction for spectral sensitivity of the multiplier phototube over the integrated emission spectrum, the relative quantum efficiencies at the λ_{max} values of the emissions produced by the PAN and O_3 reactions, 0.35 and 0.79, respectively, were applied. From these data, the chemiluminescence efficiency of the PAN reaction was calculated to be approximately 10 times greater than the corresponding ozone reaction.

A technique is being devised for measuring atmospheric concentrations of PAN. The procedure involves measuring the I_{665}/I_{500} filter intensity ratio as a function of the mole fraction of PAN relative to ozone. The percentage of PAN with respect to ozone for an unknown mixture could then be determined from this function. It therefore would be possible, by this method, to calculate absolute concentrations of PAN in ambient air, if absolute concentrations of ozone were known from independent measurements. Alternatively, of course, the detection system could be calibrated with respect to PAN. The results of this work will be published in the near future.

Although it has not been emphasized, the possible application of chemiluminescence from the ozone-amine reaction as a potential atmospheric monitor for ozone should not be disregarded.

The purpose of this work was to propose a new and potentially useful method for atmospheric detection of PAN and not to identify the luminescing species or identify reaction products in either of the described chemiluminescent reactions. However, research is now in progress dealing with these aspects, in addition to a kinetic analy-

sis of the two reactions. The reaction of various tertiary amines and sulfides are also being examined for chemiluminescence efficiency.

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Note Added in Proof. Chemiluminescence generated by bubbling PAN through a solution of triethylamine in acetone (1% V/V) was approximately twice as intense as that produced in the vapor phase reaction. The results were more reproducible in the liquid phase than in the vapor phase. Therefore, the liquid phase chemiluminescence seems to be more suitable for atmospheric monitoring applications.

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NOTES

Removal of Mercury from Aqueous Solutions by Nitrogen-Containing Chemically Modified Cotton

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■ Four chemically modified cotton celluloses were investigated for effectiveness in sorbing mercury (Hg^2) from aqueous solutions. Effectiveness of these compositions was due to amine units of the following types: ethylenimine network polymer formed in the fibers, polyethylenimine sorbed on the filters, 2-diethylaminoethyl substituents in the cellulose, and 2-aminoethyl substituents in the cellulose. Cotton celluloses modified with 2-diethylaminoethyl or 2-aminoethyl substituents were the more effective compositions at concentrations of mercury above 1000 ppb. Cotton cellulose containing ethylenimine network polymer was most effective on the basis of the weight of the cellulosic composition. Sorbed mercury can be readily removed from the chemically modified cottons for recovery of the former and reuse of the latter.

Mercury may be removed from aqueous media by precipitation as the sulfide (Deriaz, 1963), by use of ion exchange resins (Koch and Biebing, 1969; Scholten and Prielipp, 1963; and Law, 1971), by reduction and separation as metallic mercury (*C&EN*, 1970), and by sorption on proteins such as wool (Friedman and Waiss, 1972).

This paper describes the effectiveness of four different chemically modified cotton celluloses for the removal of mercury from aqueous solutions. Unmodified cellulose is ineffective.

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Experimental

Preparation of Cotton Impregnated with Cross-linked Polyethylenimine (CPEI). A prepolymer was prepared by allowing a mixture of 25 grams (0.25 mole) of 1,2-dichloroethane and 75 grams (1.75 moles) of ethylenimine to react for 16 hr in a water bath maintained at 25°C. Caution is exercised to control polymerization at this stage by efficient removal of heat. Cotton fabric impregnated with ethylenimine network polymer formed in situ was prepared as described by Roberts and Rowland (1971). The fabric was subjected to two cycles of immersion in a 20% ethanolic solution of the prepolymer and passed through squeeze rolls to a wet pickup of 95%. The impregnated fabric was allowed to dry and cure for 16 hr at room temperature. The cured fabric was washed in flowing tap water for 30 min and line-dried at room temperature. The add-on was 16%; the moisture content was 7.55%, and the nitrogen content was 2.75% on the dry basis. Aqueous solutions of the prepolymer may be used in place of ethanol solutions with similar results. Boiling the final fabric in water for 5-10 min increases its efficiency in removing mercury from aqueous solutions.

Preparation of O-(2-Diethylamino)ethyl (DEAE) Cotton. The DEAE cotton was prepared by subjecting cotton fabric to two cycles of immersion in a 1.0M solution of *N,N*-diethylaziridinium chloride (DAC), prepared as described by Roberts et al. (1971), and by passing the resultant material through squeeze rolls to a wet pickup of

115%. The wet fabric was then immersed in a 1.0M solution of sodium hydroxide at 25°C for 45 min with occasional agitation as described by Rowland et al. (1969). The fabric was then washed in flowing tap water for 30 min and line-dried. The moisture content of the modified fabric was 4.0% and the nitrogen content was 0.29% on the dry basis.

Preparation of *O*-(2-Aminoethyl) (AE) Cotton. The AE cotton was prepared by the procedure of Reeves and Guthrie (1953). Cotton fabric was subjected to two cycles of immersion in a solution containing 20 grams of 2-aminoethylsulfuric acid and 80 grams of a 37.5% solution of sodium hydroxide and to passage through squeeze rolls to a wet pickup of 159%. The fabric was heated at 130°C for 15 min on steam-heated rotating cans. The treated fabric was washed with cold water and then with hot (85°C) water; there followed a rinse with dilute acetic acid, dilute ammonium hydroxide, and finally, water, prior to drying on a tenter frame; the fabric contained 0.64% nitrogen. This fabric was subjected to a second treatment in exactly the same manner; the finished product contained 1.9% nitrogen on the dry basis.

Preparation of Cotton Impregnated with Polyethylenimine (PEI). This procedure, conducted according to the method of Wade et al. (1972), involved subjecting the fabric to two cycles of immersion in a 10% (W/W) aqueous solution of PEI 600 (average molecular weight 600,000) and then passing the material through squeeze rolls to a wet pickup of 120%. The fabric was dried successively at 80°C and 140°C for 4 min each. It was machine-washed 10 times (to ensure removal of all loosely bound PEI) and line-dried. The nitrogen content was 1.11% on the dry basis.

Separation of Mercury from Aqueous Solutions by Chemically Modified Cottons. For removal of mercury from aqueous solutions, the modified cottons were generally employed in the chopped form (ground in a Wiley mill to pass a 20-mesh screen) unless otherwise noted. The weight of modified cotton sample was such that the total nitrogen involved in each case was the same. The modified cotton was suspended in 500 ml of aqueous solution containing the mercury salt unless otherwise noted and shaken for 16 hr at room temperature. The modified cotton was removed by filtration and the filtrate was analyzed for mercury by a flameless atomic absorption technique.

Removal of Mercury from CPEI Cotton. A sample of 0.3 gram of chopped CPEI cotton was shaken for 16 hr with 1500 ml of water containing 5000 ppb of mercury. At the end of this time, the CPEI cotton was collected on a sintered glass filter and air-dried. The filtrate was analyzed for mercury. The CPEI cotton was divided into three 0.1-gram portions and placed in coarse sintered glass filters, 11 mm in diameter. The cotton in one filter was washed with 25 ml of 5% (W/W) sodium citrate solution; a second sample was washed with 25 ml of a 5% solution of disodium ethylenediaminetetraacetate (EDTA); and a third sample was washed with 25 ml of a 5% solution of sodium thiocyanate. In each case the wash solution was analyzed for mercury.

In similar experiments, the CPEI cotton samples containing adsorbed mercury were shaken for 16 hr with 5% solutions of sodium citrate, EDTA, and sodium thiocyanate, prior to filtration and analysis for mercury in the filtrate.

Results

The effect of the ratio of CPEI cotton to the volume of mercuric chloride solution on the efficiency of removal of

mercury is shown in Figure 1. The limiting volume of solution for effective reduction of mercury from 100 ppb to a level below 10 ppb by 0.10 gram of CPEI cotton is about 200 ml. The amount of mercury sorbed per 0.1 gram of CPEI cotton varies from 0.1 gram (from 2000 ml) to 0.006 gram (from 63 ml).

The rate of adsorption of mercury from solution is rapid; 1.0 gram of CPEI cotton reduced the mercury content in 2000 ml of mercuric chloride solution containing 98 ppb of mercury to a minimum (6 ppb) in 2 hr. Further contact time had no effect in lowering the mercury content of the solution.

Chopped CPEI cotton was much more efficient in the adsorption of mercury than fabric. This is illustrated in Figure 2 wherein 0.1 gram of modified cotton is employed in each case. This difference is attributed to a lower degree of accessibility of the amino groups in the fabric form due to mechanical restrictions in that composition.

The adsorptions of mercury from HgCl₂ solution by *O*-(2-diethylamino)ethyl (DEAE) cotton, *O*-(2-aminoethyl) (AE) cotton, and polyethylenimine (PEI) cotton are also shown in Figure 2. In each instance the quantity of chopped fabric used was such that the nitrogen content was approximately 0.028 gram (i.e., 0.10 gram of CPEI cotton, 1.0 gram of DEAE cotton, 0.15 gram of AE cotton, and 0.25 gram of PEI cotton). The DEAE, AE, and PEI

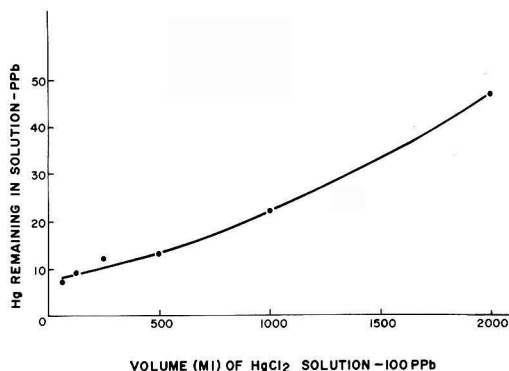


Figure 1. Effectiveness of 0.10 gram of chopped CPEI cotton in removing Hg² from various volumes of solution containing 100 ppb of Hg² as HgCl₂

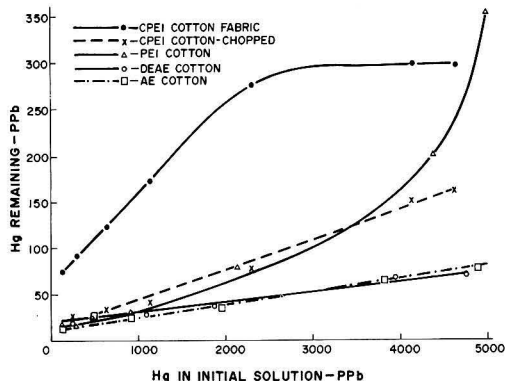


Figure 2. Comparison of the effectiveness of chopped AE, DEAE, PEI, and CPEI cotton and CPEI cotton fabric in the removal of Hg² from 500 ml of aqueous solutions of HgCl₂

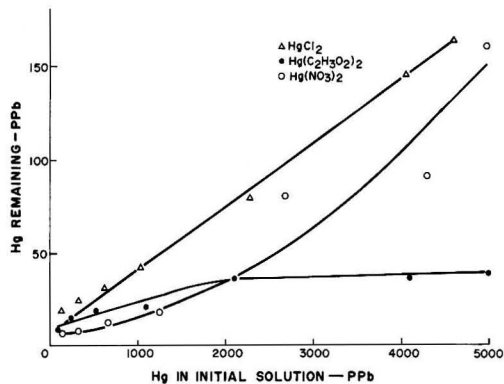


Figure 3. Effectiveness of 0.10 gram of chopped CPEI cotton in the removal of Hg^2 from 500 ml of solutions of Hg^2 in the form of the acetate, nitrate, and chloride

cottons all showed about the same effectiveness of adsorbing mercury from solutions at low concentrations of mercury. The effectiveness of DEA and AE cotton were about equal over the range of concentrations examined.

The results of removal of mercury from aqueous solutions of mercuric acetate, mercuric nitrate, and mercuric chloride with chopped CPEI cotton are illustrated in Figure 3. The CPEI cotton was more effective in removing mercury from solutions of mercuric acetate and mercuric nitrate than from solutions of mercuric chloride at low concentrations (up to 2000 ppb). The extent of removal was about equal for the chloride and nitrate salts of mercury at 5000 ppb, but much greater at this concentration for the acetate salt.

CPEI cotton may be regenerated for the recovery of mercury and reuse of the modified cotton as shown by the results in Table I. The regenerating agents tested were sodium citrate, EDTA, and sodium thiocyanate. These were checked by elution and equilibrium methods. The data in Table I indicate that EDTA is far superior to the other two regenerating agents and that the elution method is superior to the equilibrium method.

Discussion

The four chemically modified cotton celluloses examined in this exploratory study represent substantially different amine-modified celluloses with nitrogen contents differing by a factor up to 10. The amine groups are primary in AE cellulose, tertiary in DEAE cellulose, and mixed primary, secondary, and tertiary in CPEI and PEI celluloses. The amine groups in AE and DEAE celluloses are isolated and independent of one another, whereas those in CPEI and PEI celluloses are aggregated in polyethylenimine chains and might be expected to be effective in pairs for coordination of mercury or other heavy metals.

DEAE substituents were introduced in the presence of 4% sodium hydroxide without significant change in the crystalline structure of the cellulose. AE substituents were introduced in the presence of 30% sodium hydroxide with penetration and decrystallization of substantial portions of the crystalline structure. PEI cellulose was formed by simple sorption of PEI onto internal and external surfaces of the cellulose fibers without change in structure. CPEI cellulose was formed by deposition of ethylenimine network polymer internally and externally on the cellulose fibers without change in the structure of the cellulose.

Table I. Removal of Mercury from CPEI Cotton (0.1 Gram)

Method	Hg adsorbed on cotton, mg	Hg removal from cotton, %		
		Sodium acetate	EDTA	Sodium thiocyanate
Elution ^a	2.76	0.60	93.00	3.70
Equilibrium ^b	2.89	0.08	49.50	2.00

^a The elution required 30 min.

^b The CPEI cotton containing the absorbed mercury was shaken for 16 hr in the solution.

Despite the numerous differences among the chemically modified cotton celluloses, their performance in removing mercury from dilute aqueous solutions was remarkably similar when the various compositions were employed in quantities to provide equivalent numbers of amine groups. At higher concentrations of mercury (e.g., 3000 ppb) DEAE and AE celluloses were substantially more effective than PEI or CPEI celluloses. These results are consistent with the expectation that most, if not all, of the amine groups in the two former compositions are accessible to mercury, whereas only fractions of the amine groups in the latter two compositions are accessible and effective. However, this remains to be established in studies of these chemically modified cotton celluloses in which the amine content is varied over a wide range for each type of composition.

Although chemically modified cotton celluloses might be employed to remove mercury from solutions at any concentration, it appears that these compositions may be most effectively employed to remove mercury from solutions containing 100–1000 ppb. In this range, it is questionable that the present chemically modified celluloses are significantly different from one another when employed in amounts which provide equivalent numbers of amine groups. On the other hand, at equal weights of chemically modified celluloses, the effectiveness is proportional to the amine (N) content—i.e., in this set of compositions, CPEI cellulose > AE cellulose > PEI cellulose > DEAE cellulose.

The chopped form of the foregoing chemically modified celluloses can be made directly by treatment of the particulate form of cellulose. Pure cellulose such as cotton fibers or crude cellulose wastes, such as peanut hulls, may be, and have been, employed as substrates for reaction.

The foregoing chemically modified celluloses in fabric form offer intriguing possibilities such as for operation of a continuous belt of fabric to remove mercury from an industrial effluent stream and to regenerate the mercury in a concentrated solution. The operations in continuous cycle are: immersion of fabric into the mercury-containing stream and passage through squeeze rolls to remove excess solution, immersion of fabric in a regenerating bath and passage through squeeze rolls, and wash or rinse of the fabric to remove the regenerating agent prior to repetition of the cycle.

Acknowledgment

The authors are indebted to B. Piccolo and N. M. Morris for measurements of concentrations of mercury.

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CORRESPONDENCE

Identifying Sources of Lead Contamination by Stable Isotope Techniques

Sir: In a recent paper, Rabinowitz and Wetherill (1972) claim that horse fatalities near Benicia, Calif., were due in part to lead residues from smelter operations and in part to atmospheric lead contributed from automotive exhausts. This conclusion is untenable, based on historic and biological considerations.

Environmental contamination in the Benicia area has been the subject of controversy since the last century. By 1913, the matter had reached such a point that the U.S. Bureau of Mines was asked to investigate complaints by local residents about air quality and to find the reason for fatalities among horses grazing in the area. The Bureau of Mines (1915) attributed the problem to the smelter operations a few miles to the west at Selby. Since 1883, this plant had emitted large concentrations of lead and other toxic substances, resulting in contamination of the air and soil and vegetation in that area. Obviously leaded gasoline played no part in causing the problem.

In recent years, the same problem has recurred, with additional horse fatalities reported. It seems obvious that the soils in this area have been heavily contaminated with lead and other heavy metals from decades of continuing exposure to smelter emissions. It is known that soils very high in heavy metals can yield vegetation with relatively high metal content. An animal whose main source of food is such vegetation will obviously ingest large quantities of these metals, and fatalities may result.

Similar problems have occurred elsewhere in the vicinity of smelters. Examples are Trail, B.C. (Schmitt et al., 1971) and St. Paul, Minn. (Hammond and Aronson, 1964). Here, too, horse fatalities have been reported. Careful investigation has shown that vegetation containing lead emitted by the smelters caused the problem.

Claims that leaded gasoline is fully or partly responsible for these occurrences are refuted by the fact that horse fatalities of this type never occur except in the vicinity of smelters or other industrial sources of high lead emissions. If automotive exhausts were contributors to the problem, one would expect to observe such problems near busy highways, far from smelters. Yet no such problems exist. Further, if automotive exhaust contributed dangerous amounts of lead to the atmosphere, the health of other animals and humans would be threatened. Yet no such observations have ever been made, despite recent massive efforts to identify hazards due to exposure of humans to automotive exhaust lead.

That the authors have reached an unjustified conclusion is also clear from biological considerations. Simple calculations show that lead burned in gasoline cannot be a con-

tributor to the Benicia problem. The authors report that concentrations of lead in grass in the pastures near the smelter range from about 700-6000 ppm (dry basis). Assuming 3000 ppm as an average, and recognizing that a horse eats daily about 21 kg of dry forage/kg body weight (NRC, 1972), we see that a horse grazing in this pasture would ingest about 60,000 µg of lead/kg of body weight. This amount is 35 times the toxic dose (NRC, 1972) and would easily explain the horse deaths.

The amount that could reasonably be absorbed from the air because of lead emitted from automobiles is completely insignificant in comparison. Although the authors surprisingly omit lead-in-air data for the pasture areas, we can use an estimate of 2 µg/m³ of lead in air due to cars, which would almost surely be on the high side. A horse's breathing rate is about 0.3 m³/kg of body weight per day. If 37% of the lead inspired is absorbed (NRC, 1972)—a more accurate estimate of this figure we believe would be 15% (Lawther et al. 1972)—only 0.2 µg lead/kg of body weight would appear in the horse's blood due to breathing airborne lead from cars. On the other hand, the amount of lead absorbed into the blood daily owing to eating the contaminated forage mentioned above would be 1200 µg/kg of body weight. (This assumes that 2% of the 60,000 µg is absorbed through the gut—10% is estimated for humans.)

Thus the relative contribution of smelter lead vs. automotive lead to the horse's blood would be 1200/0.2, or 6000 to 1, hardly the equivalent of the 1 to 1 ratio deduced by the authors. In order to approach the 1 to 1 ratio, the lead in air value would have to reach 12,000 µg/m³. Clearly this is beyond the realm of possibility.

The author's conclusion that the lead in the horses comes half from the smelter and half from gasoline apparently derives from the following data:

	206/204 ratio
Horse lead	17.7
Smelter lead	17.3
Automotive lead	17.9

But the authors also show that gasoline lead (measured in Missouri) has a ratio of 18.5. There is no reason to suppose that gasoline sold in Missouri has a 206/204 ratio substantially different from gasoline sold in California, since lead antiknock plants in the U.S. are located with little relation to the source of ore or the area where the product is sold. Given the variability of gasoline lead between 17.9 and 18.5, it appears that the variations which

form the basis of the authors' conclusions are too small to justify their conclusions.

Other scientists using isotope ratios for identifying sources of lead have also drawn erroneous conclusions. For example, Chow (1970) concluded from his work that lead in gasoline is of the Tertiary or older model age, and that little of it is made from Missouri ores. Yet manufacturers' records show that a substantial portion of lead ore used by at least one U.S. antiknock manufacturer derives from Missouri, and the same is probably true of the other manufacturers!

In the Benicia case, the contamination of the soils with smelter emissions for nearly a century has no doubt caused wide variations in isotopic composition of lead in those soils, depending on the sources of ore refined, the wind directions, and the extent to which soils in those areas have been turned over. A few measurements of the isotopic composition of soil lead or grass lead cannot accurately reflect the exposure of horses who have been grazing there for extended periods of time.

In general, the assumption that there are fixed, distinct isotopic ratios for gasoline-derived lead or soil lead is fallacious. Techniques using isotope ratios certainly have application, but only in limited cases. The Benicia case is not one of these situations, and the conclusions of Rabi-

nowitz and Wetherill as to the sources of lead poisoning are clearly undermined by the historic and biological facts that they failed to consider.

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Sir: We are well aware of the historical and widespread problem of lead poisoning of livestock from smelter effluent, as discussed by Rifkin and Ter Haar. There is no doubt that lead smelters are capable of introducing to the surrounding environment lethal levels of lead contamination, without significant contributions from other sources. The purpose of our short discussion was to evaluate the usefulness of lead isotopes in distinguishing between different sources of lead contamination. We investigated whether in this particular case and for these particular horses, this smelter was the sole source of lead to the poisoned horses or whether it was one of a number of isotopically distinguishable sources. Our data demonstrate that in this locale the smelter was one of two or more contributing sources.

As discussed in our paper, we recognized that neither the smelter emissions, nor local TEL have fixed isotopic compositions and certainly did not make the assumption, as stated by Rifkin and Ter Haar, that "there are fixed, distinct isotopic ratios" for these sources. It was necessary to establish these isotopic compositions for the time period under consideration. As explained previously, this was done by analysis of the lead isotopic composition and concentration in samples of annual grass selected to represent essentially pure smelter lead or automotive (TEL) lead. Since the samples were selected in this way, their lead concentrations cannot be used to estimate the average amount of lead consumed by the horses from these sources.

The three horses studied had not grazed on these pastures for "extended periods of time," but only seven to nine months, almost entirely just prior to our sampling. Therefore the isotopic composition measured may be expected to represent that contributed by the smelter during that interval, regardless of whether the smelter pro-

duced lead of different isotopic composition at some time in the past. As found by Dedolph et al. (1970), and confirmed by Rabinowitz (1972) for this particular species, the contribution of soil lead to the edible portion of the grass was negligible relative to the airborne component for the grass and soil lead concentrations under consideration. In considering the Benicia pasture grasses in particular, Mueller and Stanley (1970) and Rains (1971) also concluded that very little of the lead in the tops of the grasses is from the soil. Our isotopic analyses of grass were determined on the entire plant eaten by the horses, including the stems. The concentrations of lead in the soil and the grass at the pastures are similar. Therefore, although horses forage in such a way so as to ingest some soil, they consume more grass than soil, and the possible contribution of older lead from the soil is not very important.

The biological questions raised by Rifkin and Ter Haar go beyond the initial scope of our investigation, but we believe our published data and subsequent analyses may help to answer these questions. The quantity of lead in these horses is not as great as Rifkin and Ter Haar's estimates would suggest. Isotope dilution measurements of total lead content of bones, livers, and kidneys indicate 6-16 $\mu\text{g/g}$ on a fresh weight basis. Isotopic abundance ratios identify about half of this lead as coming from the smelter and eaten by the horses with their pasture grass. Measurements of a control group of horses which died of other causes in suburban Los Angeles, and which probably were exposed to similar quantities of automobile exhaust as the Benicia horses, showed concentrations of 1-5 $\mu\text{g/g}$. This is about one quarter as much as the poisoned horses and it is plausible that this represents about as much lead as was in the horses' bodies before they were subjected to the additional exposure at these pastures.

So, in effect, the biological question raised by Rifkin

Table I. Lead Concentrations Near Benicia, Calif.

Description	Miles from smelter	Lead conc., ppm	Atomic ratios	
			206/204	206/207
Liver	5.3	6.5	17.86	1.183
Bone	5.3	16.4	17.75	1.184
TEL residue	6.2	557,000	18.02	1.185

and Ter Haar is that of the source of the remaining one quarter of the lead found in the bodies of these horses.

As discussed in a recent report by the California Air Resources Board (1972), the most recent study of this problem in the area was initiated by a large number of horse deaths on the Wesner ranch, 8.5 km downwind from the smelter. This report states that residues from the disposal of tetraethyllead were dumped at two sites, one 1.9 km and the other 2.8 km from the Wesner pasture. It is also stated that representatives of the Ethyl Corp. measured organic lead vapor concentrations of more than 2000 $\mu\text{g}/\text{m}^3$ at the dumping sites and 248 and 428 $\mu\text{g}/\text{m}^3$ at the Wesner pasture at the time the horse deaths occurred. One of the three horses studied in our previous report was from this pasture. We have subsequently measured (Table I) additional samples of a horse, diagnosed as having died of lead poisoning at the Wesner ranch, and TEL residues from one of these disposal sites. The horse results are similar to those reported previously; the TEL data are similar to the automotive lead data. Therefore, at least for the Wesner horse deaths, our previous suggestion appears to be substantiated that the source of the additional component of nonsmelter lead found in the horse tissues was either finer particles of automotive exhaust or TEL vapor. We have been unable to obtain sufficient data on the previous lead exposure history of the two non-Wesner horses to identify the source of their nonsmelter component.

It may be surprising that these relatively low tissue concentrations are associated with such high values of exposure to smelter and tetraethyllead. This, however, gets into problems of physiology and veterinary medicine entirely beyond our competence, and probably beyond that of present knowledge. In collaboration with Joel Kopple, we are currently carrying out controlled studies of human lead metabolism. Interpretation of these horse tissue concentrations would require similar studies of horses. It is

certainly not our intention to take an alarmist position, as much harm can result from overreaction to hypothetical environmental hazards. Nevertheless, the relatively small factor (~ 4) found between concentrations of lead in suburban Los Angeles horses and those in the Benicia area, together with the typical high concentrations of lead in grass (200 $\mu\text{g}/\text{g}$ dry wt.) found 300 meters from any roads in the Los Angeles area, suggests that further consideration of possible incipient toxic effects, other than those associated with smelters, should be considered. For example, horse owners could be advised to supplement the diet of their animals with forage from nonurban areas.

We find the statements by Rifkin and Ter Haar that there is no reason why gasoline lead in Missouri should be different from that in California difficult to reconcile with their (correct) statement that gasoline lead has no fixed and distinct isotopic composition. The fact is that the isotopic composition of gasoline lead *does* vary both in time and place, certainly as a consequence of TEL manufacturers' making use of different sources of lead. We have no access to the manufacturers' records which would be needed to predict what should be found at a given time and place. We can only measure what is there. It would be most interesting if relatively pure Missouri lead with its characteristically high $\text{Pb}^{206}/\text{Pb}^{204}$ ratio were to be used as the principal source of gasoline lead in some area, as this would provide a more easily identifiable source than those found heretofore.

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INDUSTRY TRENDS

Ralph E. Phillips, Inc. (Los Angeles, Calif.), consulting engineers, has announced the formulation of an affiliate, Scientific Environmental Consulting Corp. (SECO). SECO will specialize in preparing environmental impact statements.

General Electric Co. has acquired a process license from Ecology, Inc. (Brooklyn, N.Y.) to use Ecology's composting solid waste conversion system. Ecology has granted GE options to purchase up to 30% of Ecology, Inc.'s outstanding shares. Under the agreement GE and Ecology, Inc. will submit joint proposals for the construction of solid waste conversion plants throughout the U.S. The plants will be operated by GE, which will also market end products of the plants.

The Heil Co. (Milwaukee, Wis.) has been awarded a \$720,000 turn-key contract by the City of Great Falls, Mont., for the design, equipment, installation, and start-up of a solid waste reduction center. The reduction center will permit Great Falls to turn wasteland into park land.

Envirotech's Buell Div. has been awarded contracts totaling \$6 million for electrostatic precipitators. Larger of two contracts is a \$4-million order from Southern Electric Generating Co., a subsidiary of Alabama Power Co., for a 1,250,000-cfm precipitator to be installed at the utility's #2 unit of the E. C. Gaston Station, Wilsonville, Ala. Buell also received a \$2 million contract from Gulf Power Co. for two precipitators. Each of the units will handle 250,000 cfm and will be installed at Gulf's Chattahoochee, Fla., Scholz plant.

The Carborundum Co.'s Pollution Control Div. has received a \$2.6-million contract for electrostatic precipitators from Boise Cascade (Portland, Ore.). The contract covers construction and installation of four dry-bottom-type precipitators at Boise's paper mills in St. Helens, Ore., and Wallula, Wash.

Universal Oil Products Co. (Des Plaines, Ill.) has signed an agreement with Chrysler Corp. to supply all of Chrysler's requirements for automobile exhaust emission control catalysts for five years beginning with the 1976-model year. UOP is building a catalyst manufacturing facility at Tulsa-Port of Catoosa, Okla. The agreement calls for UOP to supply Chrysler with a noble metal-activated monolithic catalyst.

American Can Co. (Greenwich, Conn.) has created a new energy management department to develop and implement policies, programs, and procedures for efficient utilization and conservation of energy. American Can says it's the company's intention to place energy usage considerations on a high priority level in all future company operating decisions, just as environmental considerations command high priority treatment.

Browning-Ferris Industries, Inc. (Houston, Tex.) will file a registration statement for an underwritten secondary offering of approximately 1,750,000 shares of common stock by stockholders, principally former owners of businesses previously acquired by BFI. The company will not offer any shares.

Wheelabrator-Frye, Inc., M. DeMatteo Construction Co., and General Electric Co. have signed a series of agreements for \$27-million steam raising incinerator in Saugus, Mass. Wheelabrator-Frye and M. DeMatteo Construction Co. will start construction immediately on the Wheelabrator-Von Roll energy conversion incinerator which will convert refuse to high-quality steam to be purchased by General Electric's nearby Lynn plant. Project will have initial capacity of 1200 gpd municipal and commercial refuse and is expected to be in operation by early 1975.

Envirodyne, Inc. (Los Angeles, Calif.) has signed a definitive agreement, subject to regulatory approval, to merge Saxton & Kennedy Consulting Engineers, Inc. (Spokane, Wash.) into Envirodyne Futrell, Inc., a wholly owned Envirodyne subsidiary based in Washington. The agreement calls for payment up to a maximum of \$313,000 to be made primarily in Envirodyne common stock, depending upon future Saxton & Kennedy earnings levels.

Chemical Construction Corp. plans to begin building the world's largest facility for the production of liquefied natural gas. The plant will liquefy 1 billion scf of gas/day in Arzew, Algeria, for the U.S. East Coast market. The overall project, the largest yet approved for the import of LNG anywhere in the world, is valued at approximately \$350 million for Chemico. The daily energy equivalent of LNG produced at plant is 200,000 barrels of crude oil, or 49,000 tons of coal.

Dearborn Chemical Div. of Chemed Corp. has formed Dearborn Environmental Engineers, an expansion of its Municipal-Industrial Waste Treatment Div. The organization will specialize in providing complete laboratory services, pollution control surveys, and treatability studies to governmental bodies and industries facing waste water treatment problems. The group will be headquartered in Dearborn's Lake Zurich, Ill., research and analytical laboratories.

Predicasts, Inc. (Cleveland, Ohio), a business information research firm, has requested appropriate authorities in Washington to take action against the current practices of Chase Manhattan Bank in commercial sale of information and consulting. Predicasts believes these practices are improper, contrary to the public interest, and represent unfair competition.

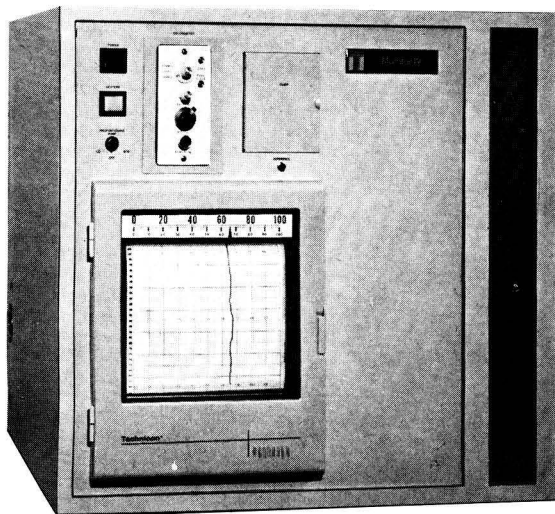
Rexnord, Inc., formerly Rex Chainbelt, has combined all of its environmental control operations into a new wholly owned subsidiary, Envirex, Inc. The new subsidiary will have three operating units, the water quality control division, the newly formed air pollution control division, and the environmental sciences division, and a group made up of scientists and technical staff.

Kennecott Copper Corp. has awarded a \$2-million contract to the Kellogg Corp., an affiliate of The M. W. Kellogg Co., for construction of a 750-ft chimney at its McGill, Nev., smelter. The chimney is part of the company's program to meet federal and state ambient air quality standards. The project is under way and will be completed in approximately two years.

Holley, Kenney, Schott, Inc. (Pittsburgh, Pa.) has received a turn-key contract from the Jessop Steel Co. for a fume and dust control system at Jessop's Washington, Pa., specialty steel making plant. The system will trap airborne particulate matter generated by Jessop's three electric arc furnaces.

Combustion Engineering, Inc., through its subsidiary, Lummus Co., has been awarded a \$30-million contract to design, engineer, and construct a 125-million scf synthetic natural gas plant for the South Jersey Gas Co. The proposed plant, to be located in Gloucester County, N.J., will use technology based on the catalytic rich gas process.

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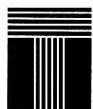
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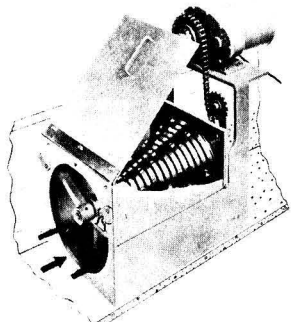
ACIDITY	HYDRAZINE
ALKALINITY	HYPOCHLORITE
ALUMINUM	IRON
AMMONIA	MAGNESIUM
CARBONATE	MANGANESE
CAUSTIC (NaOH)	NICKEL
CHLORATE	NITRATE + NITRITE
CHLORIDE	NITRITE
CHROMIUM	PEROXIDE
COLOR	PHOSPHATE, ORTHO
COPPER	PHOSPHATE, TOTAL INORGANIC
CYANIDE	SILICA
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Flowminutor

A flowminutor is designed for efficient and economical reduction of solid particles in liquid waste. The machine utilizes cutters positioned throughout the screen periphery and secured by a threadless lock. This provides an even scissor-cutting action and increases efficiency. Enviro-Care Co. **61**

Sewage ejector

A high-capacity, heavy-duty (6-in.) sewage ejector line offers 4-in. spherical solids-handling capabilities. Designed for sewage lift station and industrial sump applications that require large-diameter solids handling and high capacities, the new ejector will operate in liquids reaching 160°F. The pumps have a 5-in. suction port and a 6-in. discharge. Available in 18 models. Peabody Barnes Inc. **62**

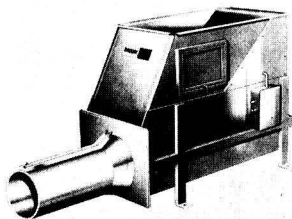


Analytical system

A portable analytical system is suitable for municipal and field pollution control work. The analyzer consists of new premeasured and prepackaged chemical reagents that are combined into stable, single formulations and packaged in single-use, optical glass vials. The unit, which has direct read-out meter scales for each test, operates on both ac and rechargeable batteries. Hydrodyne, Inc. **63**

Chlorination process

A self-regulating, maintenance-free system for chlorination of waste water can process up to 100,000 gal/day. Called the Sanuril Wastewater Treatment System, it consists of a non-mechanical chlorinator that uses a sanitizing agent in tablet form. The simple, one-piece construction requires only inlet piping, with no electrical power, wiring, bypasses, or other piping. Diamond Shamrock Corp. **64**



Trash compactor

A trash compactor reduces high volumes of trash and ejects the compacted material into portable bags or barrels automatically. Designed for use in buildings where space or pickup facilities do not permit the use of standard trash containers, the unit reduces trash volume by an average ratio of 10 to 1. Maxon Industries, Inc. **65**

Separation coagulant

A cationic, polymer-based, liquid coagulant for solids/liquid separation is ready for use in municipal and industrial waste water systems. The product may be used as a primary coagulant or as a coagulant aid in conjunction with inorganic primary coagulants. It is effective over a wide solids and pH range and can be used in filtration, sedimentation, flotation, and centrifugation processes. Calgon Corp. **66**

Ion monitors

Automatic selective ion monitors for on-line pollution monitoring are capable of continuous operation in difficult environments. The instruments can serve as reliable pollution monitors in potable water supplies, rivers, and effluents. Each model in the series uses a different selective electrode as the sensing element. Caroe Marketing, Inc. **67**

Water analyzer

A multiparameter in-situ water analysis instrument system is suitable for both automatic and survey monitor

applications. Analyses for D.O., conductivity, pH, ion concentrations, or ORP and temperature can be made simultaneously by the system to depths of 100 meters in either fresh, salt, or estuarine waters. The battery-powered surveyor is a portable, all-weather field instrument designed for both boat and shore operations. Hydrolab. **68**

Incubation

Unit for low-cost adaptation of any type household refrigerator into precision low-temperature incubator provides close temperature control and safe long-term operation. No modification of refrigerator is necessary and the unit's electrical system is fully grounded. Heaters are ceramic-covered and of low wattage density. Temperature range from 5-50°C is dial adjustable. N-CON Systems Co., Inc. **69**

Compactor

Stationary compactor crushes hard-to-handle industrial refuse such as lumber, barrels and cans, pallets, and bulky nonburnables with 32 tons of compaction power. System uses horizontal ram-type compactor which pushes block into sturdy roll-on, roll-off container. Auto Pak **70**



Sealant system

A new sealant system replaces mercury in the reaction-driven rotary distributor of sewage treatment plant trickling filters. The system features a newly developed sealant that is pumped into the distributor arm center-column housing after the mercury has been removed. It is effective in both arctic and desert operations. Chemola Corp. **71**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

Electrostatic precipitator

Completely self-contained electrostatic precipitator will remove smoke, mist, dust, and other pollutants from the air. The unit can be incorporated into duct work or suspended free from the ceiling over particular problem areas. Two models are available which will handle 1500 or 3000 cfm. General Resource Corp. 72

Vibrating screen

New line of 60-in. diameter screens is made of stainless steel wire cloths attached with polymeric bonding. Diameter of 60 in. compliments line of screens available previously only in 30- and 48-in. diameters. Multi-Metal Wire Cloth, Inc. 73

Moisture meter

Moisture content of liquids such as fuels, solvents, and oils as well as of gases and solids can be measured on direct-reading instrument. Readings can be made in less than 1 min. No standardization is required. Multirange instrument allows measurements to be made as low as 0-300 ppm water, as high as 0-0.6% water. Sensitivity is 50 ppm water. Meter is portable, lightweight, and can be line-operated in the lab or battery-operated in the field. Ericson Instruments 74

Atomic absorption

New atomic absorption spectrophotometer is top-of-the-line model which allows better analytical performance. Readout electronics uses signal averaging and integration to give optimum precision and detection limits. Spectrophotometer permits direct readout in concentration on electrical digits when using flameless or flame sampling devices. Perkin-Elmer 75

BOD meter

Biochemical oxygen demand meter is designed for practical sewage plant applications. Unlike dissolved oxygen monitors, the unit indicates short term BOD in as little as 15 min after sample is gathered on mixed liquor or return sludge. Unit is self-contained and automatic. Badger Meter, Inc. 76

Centrifugal concentrator

New 60-in. centrifugal waste water concentrator is designed to handle large-volume hydraulic flows from 800-2000 gpm. Unit is suitable for effluent and water recycle streams from larger industrial plants. Concentrator removes suspended solids down to 10 μ . SWECO, Inc. 77

Sulfur analyzer

Atmospheric sulfur analyzer is designed for long-term unattended operation. Operating on gas chromatographic principles, analyzer separates and independently measures H₂S/SO₂ and other vapor-state sulfur compounds in gases. TRACOR, Inc. 78

The Threat of the Unseen

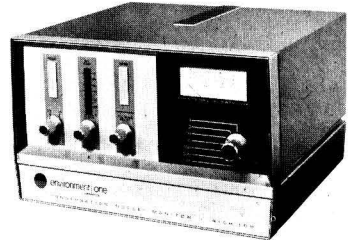
Air that looks clean may not really be clean . . . the sub-micron particles are still there . . . you just don't see them.

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NEW LITERATURE

Sound measurement. Quick-reference explanation of sound measurement for construction, mining, and industrial executives defines decibels and provides comparison ratings of common sound. Colt Industries, Quincy Compressor Div. **91**

Cooling tower. New brochure describes Type 53 Crossflow cooling tower. Shows detailed cutaway drawings of construction and includes photographs of tower's components. Also described are redwood structural frame and fan decks, fiber glass fans, and water distribution systems. Ecodyne Cooling Products Co. **92**

Standards solutions. Data sheets describing standardized solutions of 30 commonly determined metals includes compositions, catalog numbers, and prices. Samples are checked against National Bureau of Standards materials and designed for use in atomic absorption units. Fisher Scientific Co. **93**

Reverse osmosis. Two-page illustrated bulletin describes operating details of advanced Helical Tubular Segment (HTS-100) reverse osmosis unit. Bulletin contains details of tubular membrane and flow diagram. Philco Ford Corp. **94**

Materials handling fans. Bulletin describes centrifugal fans used primarily for pneumatic conveyance of materials, dust collection, and fume removal. Fans with capacity rated to 86,900 cfm, pressures to 20 in., and temperatures to 1000°F are available. Bulletin includes application data, selection chart, accessories, and performance charts. Aerovent Inc. **95**

Exhaust analysis. Literature describes features and operation of system for analyzing vehicular exhaust emission. System features various modular components and options for meeting 1972-76 Federal Testing Procedures. Environmental Tectonics Corp. **96**

Catalog. Folder describes grooved piping designed for power plant applications. Piping is applicable to basic water, air, and vacuum and drainage systems, as well as pollution control systems, fly ash slurry lines, cooling water, SO₂ removal, powdered coal conveyor piping, and other uses. Victaulic Co. of America. **97**

Diaphragm pumps. Four-page technical bulletin describes company's line of high-pressure diaphragm pumps, specifically developed for water treatment and process applications. Bulletin contains pump features and chart for selection of proper pump. Materials of instruction and ordering information are also included. Neptune Chemical Pump Co. **98**

Test equipment. One-page guide to environmental test equipment describes 18 types of cabinets, rooms, and systems. Bulletin presents abbreviated specifications for temperature, humidity, altitude, space, thermal shock, and clean environment chambers. Tenney Engineering Inc. **99**

Environmental services. New 12-page brochure describes four assistance programs available to consulting engineers and waste water treatment managers. Programs include comprehensive start-up and training for new solids handling plants, guaranteed O&M program for existing treatment plants, computerized-based monitoring and analysis systems, and quarterly inspection and maintenance services. Envirotech, Inc. **100**

Aerosols. Basic primer is designed to answer some of the most frequently asked questions about aerosols including what they are, how they are formed, why they are hazardous, how they can be controlled, and other information. Peabody Engineering Corp. **101**

Catalog. Comprehensive 72-page catalog includes a 21-page OSHA reference section which provides most current information concerning requirements for accident prevention signs and warning tags as required by OSHA. Seton Name Plate Corp. **102**

Electromagnetic water sensors. Paper discusses theory of operation and practical advantages and limitations of solid state electromagnetic water current transducers. Test data and system design graphs are included to allow a potential user to become familiar with the various tradeoffs available. Marsh-McBirney, Inc. **103**

Aerator bulletin. New aerator bulletin is constructed to aid process engineers in design and specification of company's aerator system for municipal

or industrial waste treatment. Contents include descriptive information and operation data. Kenics Corp. **104**

pH equipment. Catalog describes complete line of pH meters, electrodes, and accessories including miniature models so small one will slip into a shirt pocket. Several are digital meters offering simplified operation, and one model has readability to 0.001 unit over the entire 0-14 pH range. Kruger & Eckels, Inc. **105**

Air samplers. New 12-page brochure describes complete line of high-volume air-sampling equipment collecting particles as small as 0.01 μ . Bulletin includes description of accessory equipment including filter holders, filter paper cartridges, transformers, timers, and programmers, as well as aluminum shelters. General Metal Works, Inc. **106**

Newsletter. Environmentalists and scientists will find informative up-to-date survey of instruments and techniques for monitoring air and water pollution in company's newsletter. Current issue features articles on packaged laboratories for water and waste water analysis, "how to" information on automatic EPA titrations, and rundowns on several instruments. Fisher Scientific Co. **107**

Noise engineering. Illustrated 16-page report delves deeply into the subject of industrial noise-level criteria in relation to audiometric testing, hearing conservation, speech communication, and municipal zoning. Includes review of available modular acoustically rated components and preassembled acoustic structures and silencers with case histories. Industrial Acoustics Co., Inc. **108**

Source sampling. Booklet describes company's gaseous source sampling service. Also discusses quarterly sampling school for training monitoring personnel. Nalco Chemical Co. **109**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

BOOKS

Pollution Engineering and Scientific Solutions. Euval S. Barrekette, Editor. xv + 784 pages. Plenum Publishing Corp., 227 West 17th St., New York, N.Y. 10011. 1973. \$35, hard cover.

Interdisciplinary work offers short- and long-term engineering, scientific, and legal solutions to environmental problems. In this volume, the second in the Environmental Science Research series, authorities outline solutions to sulfur dioxide, propellant and explosive, and solid waste and noise pollution problems.

Air Pollution. D. H. Michael Bowen, Editor. v + 138 pages. American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. 1973. \$3.50, paper. \$5.95, hard cover.

Sequel to "Solid Wastes," the book contains articles on air pollution published in *Environmental Science & Technology* from 1969 through 1972. It features sections on laws and regulations, specific pollutants and standards, monitoring, control methods, and transportation.

Disposal of Refuse and Other Waste. John Skitt. xiv + 414 pages. Halsted Press, 605 Third Ave., New York, N.Y. 10016. 1973. \$21.50 hard cover.

Book is an introduction to the subject of waste disposal. It considers the design of treatment plants and future developments in solid waste management. Controlled tipping of refuse, industrial solids and slurries, incineration, and the use of intermediate treatment plants in the transfer of bulk haulage to distant sites are discussed.

Who Speaks for Earth? Barbara Ward et al. 173 pages. W. W. Norton & Co., Inc., 55 Fifth Ave., New York, N.Y. 10003. 1973. \$6.95, hard cover.

Series of lectures sponsored by the International Institute for Environmental Affairs during the United Nations Conference on the Human Environment held in Stockholm in June 1972. Each lecture deals with a different aspect of the environmental problem. Besides Barbara Ward, Rene Dubos, Thor Heyerdahl, Gunnar Myrdal, Carmen Miro, Lord Zuckerman, and Aurelio Peccei contribute.

Progress in Hazardous Chemicals Handling and Disposal. Robert H. L. Howe, Editor. viii + 244 pages. Noyes Data Corp., Noyes Bldg., Park Ridge, N.J. 07656. 1972. \$20, paper.

Book contains proceedings of symposium held in Indianapolis last year. It deals with separation methods and subsequent handling and disposal of dangerous and toxic substances. Also, panel groups discuss at length the control of toxic materials in the food industry and the disposal and burning of plastic materials.

Water and Water Pollution Handbook. Vol. 4. Leonard L. Ciaccio, xi + 630 pages. Marcel Dekker, Inc., 93 Madison Ave., New York, N.Y. 10016. 1973. \$29.50, hard cover.

Volume 4 of this multivolume treatise on water and water systems presents instrumental techniques as applied to the detection of organic and inorganic substances and radioactive nuclides in natural waters and waste effluents. Watering systems also are discussed. Author and subject indexes to all four volumes in the series are included.

Pollution Control in the Textile Industry. H. R. Jones. x + 323 pages. Noyes Data Corp., Park Ridge, N.J. 07656. 1973. \$36, hard cover.

Based largely on government reports and surveys, book attempts to clarify the ways and means open to the textile processor who must keep his pollution at a minimum. It helps the manufacturers come to terms with problems arising from the fact that although many effluent wastes from textile mills are biodegradable, treatment costs are increasing and effluent discharge requirements are becoming more stringent.

Engine Emissions: Pollutant Formation and Measurement. George S. Springer and Donald J. Patterson, Editors. xii + 371 pages. Plenum Publishing Corp., 227 West 17th St., New York, N.Y. 10011. 1973. \$28.50, hard cover.

Offers survey of the current state of engine emissions science and a guide to relevant literature in the field. Work focuses on sources and mechanisms of emission formation within combustion engines, as well

as on measurement techniques. Spark ignition and diesel and aircraft engine processes are analyzed.

Cost Effectiveness in Pollution Control. Proceedings of the Fifth Annual Northeast Regional Antipollution Conference. iv + 332 pages. Technomic Publishing Co., Inc., 265 W. State St., Westport, Conn. 06880. 1972. \$20, paper.

Book attempts to assess the nationwide cost effectiveness of the EPA's effort to improve the nation's air quality by 1976. Thirty-eight emission categories were studied, and cost/benefit ratios were determined as the measure of cost effectiveness for each category for which cost information was available. Book concludes that the overall cost effectiveness of EPA strategy is within an acceptable range.

Mercury in the Environment: An Epidemiological and Toxicological Appraisal. Lars Friberg and Jaroslav Vostal, Editors. 215 pages. Chemical Rubber Co. Press, 18901 Cranwood Parkway, Cleveland, Ohio 44128. 1972. \$22.50, hard cover.

Written under contract with EPA and Department of Environmental Hygiene of the Karolinska Institute, Sweden, the book reviews available data on mercury toxicity. It focuses on information considered of special importance in understanding the toxic action of mercury, and on quantitative information in regard to mercury's effects on human beings and animals.

Coastal Zone Pollution Management. Billy L. Edge, Editor. vi + 282 pages. Office of Industrial and Municipal Relations, College of Engineering, Clemson University, Clemson, S.C. 29631. 1972. \$8.00, paper.

Book is a reprint of speeches and papers presented at an EPA and Clemson University symposium on coastal zone pollution management held in Charleston last year. It seeks to identify the important problems that the Southeast faces in coastal zone pollution management; to explain the role of national, regional, state, and local governmental agencies; and to indicate available techniques for solution of these problems.

Environment Chemistry. Stanley E. Manahan. v + 393 pages. Willard Grant Press, Inc., 53 State St., Boston, Mass. 02109. 1972. \$6.95, paper, \$10, hard cover.

Designed as a textbook for courses dealing with environmental chemistry, it begins with the assumption that any serious attempt to solve environmental problems must involve the extensive use of chemicals and chemical processes. Organized around chemistries of the hydrosphere, the lithosphere, the atmosphere, and the biosphere, the book assumes the student has some knowledge of analytical and organic chemistry.

Natural Environments: Studies in Theoretical and Applied Analysis. John V. Krutilla, Editor. viii + 352 pages. Johns Hopkins University Press, Baltimore, Md. 21218. 1973. \$16.50, hard cover.

Contributors to the book express concern that many urgent questions of allocating and administering wild lands have been ill-explored. They seek to show that not all of the wild and scenic areas in nature need be altered in pursuit of material consumption objectives. The nine papers in the book represent a cross section

of current progress in Resources for the Future's natural environment program.

Environmental Pollution: A Survey Emphasizing Physical and Chemical Principles. Laurent Hodges. xii + 370 pages. Holt, Rinehart, and Winston, Inc., 383 Madison Ave., New York, N.Y. 10017. 1973. \$7.95 hard cover.

Book attempts to fill need for a one-volume scientific discussion of the major types of environmental pollution and their effects on man and the environment. It discusses air, noise, solid waste, and thermal and radiation pollution. Physical and chemical principles are emphasized more than biological and ecological principles. Designed as a textbook.

Directory of Environmental Information Sources. 2nd ed. Charles E. Thi-beau, Editor. ix + 457 pages. Cahners Books, 89 Franklin St., Boston, Mass. 02110. 1972. \$25, hard cover.

This in-depth directory contains current information relating to ecological problems. With more than 3700 listings, 1000 of them new, this second edition reference work organizes data from widely scattered sources. It lists both public and private organizations that deal with the

environment, as well as documents and reports, periodicals, books, filmstrips, conferences, and published bibliographies.

Waste Disposal Control in the Fruit and Vegetable Industry. H. R. Jones. x + 261 pages. Noyes Data Corp., Park Ridge, N.J. 07656. 1973. \$36, hard cover.

Based largely on authoritative government reports and surveys, book outlines ways the food processor can hold down pollution wastes. It considers in depth such topics as harvest, and delivery, food processing operations, waste treatment processes, water pollution abatement costs, and the impact of pollution control on industry costs.

Lectures in Transportation Noise. Richard H. Lyon. vii + 259 pages. Grozier Publishing, Inc., Warren Ave., Harvard, Mass., 01451. 1973. \$20, paper.

The fundamentals of acoustic theory is explored as the basis of modern technology for noise measurement, production, and control. The author develops the concept of source-path-receiver analysis and applies it to today's major transportation noise sources—aircraft, sonic booms, automobiles, trucks, and rail vehicles.



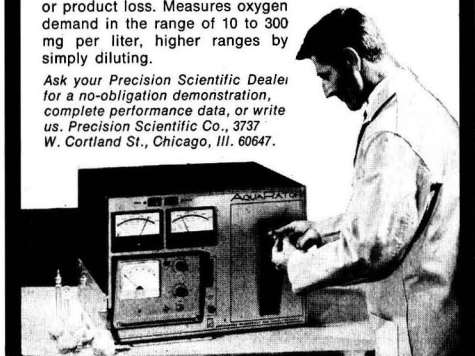
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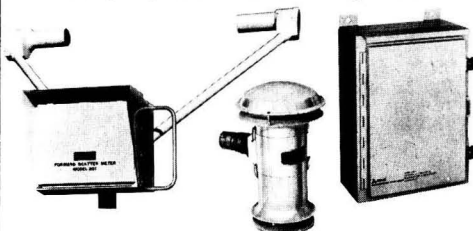
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MEETING GUIDE

June 20 Storrs, Conn.

Wetland Conference. University of Connecticut

Write: T. Helfgott, University of Connecticut, Storrs, Conn. 06268

June 20-22 Columbus, Ohio

1973 Joint Automotive Control Conference. AIAA, AIChE, ASME, IEEE, ISA, TAPPI, ITE, and SCI

Conference will emphasize application to societal, economic, ecological, and biological systems. *Contact:* ASME, 345 E. 47 St., New York, N.Y. 10017

June 20-22 Boulder, Colo.

Technical Council on Water Resources Planning and Management. American Society of Civil Engineers.

Theme is "Interdisciplinary Analysis of Water Resource Systems." *Write:* Herbert R. Hands, American Society of Civil Engineers, 345 E. 47 St., New York, N.Y. 10017

June 22-23 Dayton, Ohio

Fifth Ohio Valley Gas Chromatography Symposium. Ohio Valley Gas Chromatography Discussion Group

Contact: Ohio Valley GCDG, Attn: Jean Weaver, Station B, Box 8, Dayton, Ohio 45407

June 24-28 Chicago, Ill.

Air Pollution Control Association. 66th Annual Meeting & Exhibition

Contact: Daniel R. Stearn, APCA, 4400 Fifth Ave., Pittsburgh, Pa. 15213

June 24-29 Philadelphia, Pa.

American Society for Testing Materials. 76th Annual Meeting and Exposition

Contact: ASTM Meetings Dept., 1916 Race St., Philadelphia, Pa. 19103

June 26-29 Saskatoon, Sask., Canada

Canadian Federation of Biological Societies. Annual Meeting

Write: D. T. Armstrong, Dept. of Physiology, Univ. of Western Ontario, London 72, Ont., Canada

July 2-6 Meriden, N.H.

Oil and Other Hazardous Materials. Gordon Research Conferences

Other Gordon conferences in July include one on toxicology and safety evaluations and another on environmental sciences: air. *Write:* Gordon Research Conferences, Pastore Chemical Laboratory, University of Rhode Island, Kingston, R.I. 02881

July 3-5 Mexico City, Mexico

Nuclear Energy Conference. American Nuclear Society

Write: ANS, 244 E. Ogden Ave., Hinsdale, Ill. 60521

July 9-11 Boulder, Colo.

Salinity: A Critical Review of Causes and Control Conference. University of Colorado

Will cover causes and controls over growing salinity in water supplies. *Contact:* Bureau of Conferences and Institutes, Division of Continuing Education, University of Colorado, Boulder, Colo. 80302

July 16-19 San Diego, Calif.

Environmental Control & Life Support Conference. SAE, ASME, and others

Will cover environmental control and waste management in spacecraft and marine environmental systems. *Write:* American Society of Mechanical Engineers, 345 E. 47 St., New York, N.Y. 10017

July 17-19 Montreal, Que., Canada

1973 Summer Computer Simulation Conference. AIChE, AMS, ISA, SCI, SHARE

For details: Lawrence Sashkin, Publicity/Publications Chairman, The Aerospace Corp., P.O. Box 92957, Los Angeles, Calif. 90009

July 17-19 Seattle, Wash.

Conference on Ocean Resources as Related to Overall National Economic and Social Needs. National Oceanic and Atmospheric Administration

Write: Assistant Deputy Administrator, NOAA, Department of Commerce, Washington, D.C. 20230

July 18-20 Ann Arbor, Mich.

Symposium on Wastewater Effluent Limits. University of Michigan and others

Designed to consider material of interest to water pollution scientists and administrators connected with both government and industry, water economists, and attorneys. *Contact:* John J. Gannon, School of Public Health, University of Michigan, Ann Arbor, Mich. 48104

July 24-26 Denver, Colo.

Water Conditioning Association International. 28th Annual Convention and Exposition.

Contact: WCAI, 330 S. Naperville St., Wheaton, Ill. 60187

August 1-3 Fort Collins, Colo.

Development and Population Alternative Futures for the West. Seminar. Colorado State University

Will study the impacts and consequences of growth in the West as it affects the overall quality of life. *Contact:* Office of Conferences and Institutes, Center for Continuing Education, Colorado State Univ., Fort Collins, Colo. 80521

August 8-10 Atlanta, Ga.

1973 Cryogenic Engineering Conference. U.S. Department of Commerce

Overall theme of Energy and Environment. *Write:* Jack E. Jensen, Program Chairman, Brookhaven National Laboratory, 1 E. 4th, Upton, N.Y. 11973

August 13-15 Philadelphia, Pa.

National Conference on Environmental Engineering Education. Drexel University and others

Will formulate academic guidelines for training the next generation of environmental engineers, administrators, and technologists. *Contact:* Office of Continuing Professional Education, Drexel University, Philadelphia, Pa. 19104

August 13-17 Philadelphia, Pa.

8th Intersociety Energy Conversion Engineering Conference. ACS and others

Write: Arvin H. Smith, Thermo Electron Corp., 85 First Ave., Waltham, Mass. 02154

August 14-16 Boulder, Colo.

Symposium on Instrumentation for Monitoring Air Quality. American Society for Testing and Materials and others

Critical overview of monitoring instrument performance. *Contact:* ASTM, 1916 Race St., Philadelphia, Pa. 19103

Courses

June 21-Aug. 3 Houston, Tex.

15th Summer Session of Statistics in the Health Sciences. University of Texas

Will cover environmental health, population, and numerous other topics. *Write:* Summer Session of Statistics, University of Texas School of Public Health, P.O. Box 20186, Astrodome Station, Houston, Tex. 77025

June 22-23 Berkeley, Calif.

Airport Noise Developments. University of California, Berkeley.

Deals with developments in control and reduction of noise exposure arising from aircraft operations at and near airports. *Write:* Continuing Education in Engineering, University of California Extension, 2223 Fulton St., Berkeley, Calif. 94720

June 26-27 Madison, Wis.

Planning, Designing, and Implementing Cooperative—Areawide Solid Waste Management Systems. University of Wisconsin-Extension

Objective is to inform engineers, planners, and public works and government officials concerning the development of regionalized solid waste management systems. Fee: \$95. *Contact:* Thomas P. Kunes, University of Wisconsin-Extension, 432 N. Lake St., Madison, Wis. 53706

June 26-28 Nashville, Tenn.
Process Design Techniques for Industrial Waste Treatment. Associated Water and Air Resource Engineers, Inc.

Fee is \$150. Write: AWARE, Inc., 2002 Richard Jones Rd., Suite C304, Nashville, Tenn. 37215

July 1-6 Henniker, N.H.
Viruses in the Water Environment. Engineering Foundation

Fee: \$160. Write: Engineering Foundation, 345 E. 47 St., New York, N.Y. 10017

July 2-27 Boston, Mass.
Summer Institute on Environmental Health. Harvard University

Write: Dade W. Moeller, Harvard School of Public Health, 665 Huntington Ave., Boston, Mass. 02115

July 2-27 Oak Ridge, Tenn.
Environmental Aspects of the Radiation Sciences. Oak Ridge Associated Universities

Also institutes at later dates on applied ecology, energy sources for the future, and trace analysis for environmental pollutants. Write: L. K. Akers, Chairman, Special Training Division, Oak Ridge Associated Universities, P.O. Box 117, Oak Ridge, Tenn. 37830

July 8-14 Sherburne, N.Y.
Workshops on Environmental Concerns. N.Y. Department of Environmental Conservation and others.

Workshops designed to acquaint high school students with the major environmental problems confronting society today. Also held at later dates. Contact: Lauren Vredenburgh, Rogers Environmental Education Center, Sherburne, N.Y. 13460

July 15-20 Henniker, N.H.
Energy Research—Alternatives for Policy and Management to Meet Regional and National Needs. Engineering Foundation

Fee: \$160. Contact: Engineering Foundation, 345 E. 47 St., New York, N.Y. 10017

July 15-28 Fort Collins, Colo.
Fourth International School for Environmental Management. Westinghouse Power Systems Environmental Systems Department

Will train personnel from electric utility companies, generating industrials, and governmental agencies in the technological and legal aspects of environmental management. Write: Westinghouse Power Systems, J. H. Wright, Director, Environmental Systems Department, P.O. Box 355, Pittsburgh, Pa. 15230

July 16-20 University Park, Pa.
Machinery Noise Control by Design Seminar. Pennsylvania State University

Will cover various types of noise sources typical of machinery and means of noise reduction. Write: Pennsylvania State University, Conference Center, J. Orvis Keller Bldg., University Park, Pa. 16802

July 16-20 Denver, Colo.
Recycling of Food Processing Wastes. University of Denver

Other workshops to be held include engineering for air quality and noise pollution and control. Contact: Ray M. Wainwright, College of Engineering, University of Denver, Denver, Colo. 80210

July 30-August 10 Cambridge, Mass.
Energy: A Unified View. Massachusetts Institute of Technology

Contact: Director of the Summer Session, MIT, Room E19-356, Cambridge, Mass. 02139

August 12-17 Denver, Colo.
Process and Environmental Analytical Instrumentation. Instrument Society of America

A concurrent course, "Sampling and Sampling Systems for Process and Environmental Instrumentation," is also offered. Fee: \$300. Write: ISA, Education Department, 400 Stanwix St., Pittsburgh, Pa. 15222

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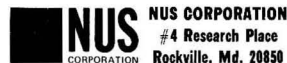
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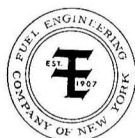
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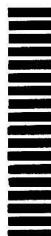
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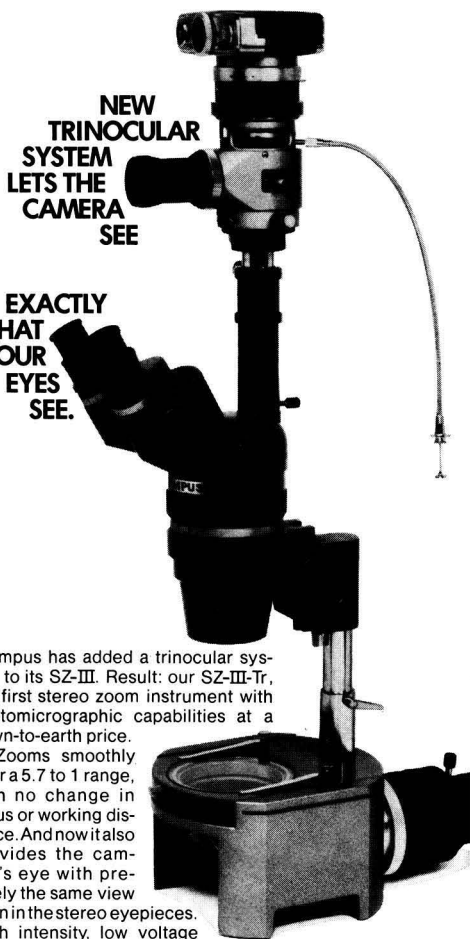
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Zooms smoothly over a 5.7 to 1 range, with no change in focus or working distance. And now it also provides the camera's eye with precisely the same view seen in the stereo eyepieces.

High intensity, low voltage light sources are available for reflected and transmitted light. Normally equipped for a magnification range of 7x to 40x; additional wide-field eyepieces and objectives are easily inserted to provide magnification as low as 3.5x or as high as 160x in seven magnification ranges. Fully compatible with the Olympus Photomicrographic Camera System PM-10 or other similar equipment.

Photomicrography with a stereo zoom microscope at modest prices... worth looking into! Write:

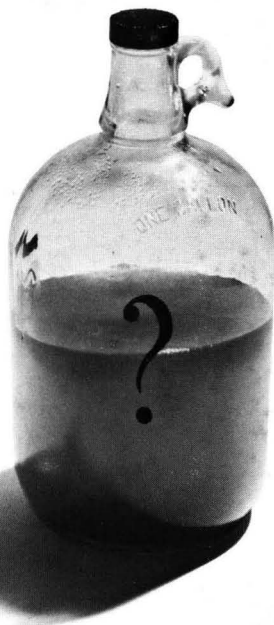
Olympus Corporation of America,
Two Nevada Drive, New Hyde Park,
New York 11040.

In Canada: W. Carsen Co. Ltd., 31
Scarsdale Road, Don Mills, Ontario.

SEEING BEYOND MAN'S VISION
OLYMPUS
Circle No. 19 on Readers' Service Card

carbon in water?

total organic carbon
volatile organic carbon
total carbon



Dohrmann's DC-50 organic analyzer makes *all* of these measurements accurately and rapidly. Based on proven methods, it avoids interferences and undesirable pyrolysis reactions that historically have resulted in significant errors.



DIRECT READOUT. Four-digit presentation shows carbon content directly in mg/liter or ppm.

No recorder needed!

DIRECT MEASUREMENT. A single sample injection gives either Organic Carbon or Total Carbon content **directly, not by difference.**

INDEPENDENT MEASUREMENT. Volatile Organics are determined separately from Total Organics to aid in source identification.

RELIABLE MEASUREMENTS. Determines important, lightweight volatiles such as low molecular weight alcohols and ketones, normally lost by acidification and sparging.

FAST: 5 minutes per determination

ACCURATE: Repeatability of ± 1 mg/liter or $\pm 2\%$

WIDE RANGE: 1 to 2,000 mg/liter (ppm) without dilution

PRICE: \$7,500, including start-up assistance and operator training

DOHRMANN Division, Envirotech Corporation, 1062 Linda Vista Avenue, Mountain View, CA 94040 (415) 968-9710.



ENVIROTECH



*EPA EVALUATED: Newsletter No. 15
Oct. 1972 AQCL, NERC, EPA
Cincinnati, Ohio 45268

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We MUST be doing something right...

All the other fellows are imitating us!

Three years ago we pioneered the use of the chemiluminescent principle in our Ozone Monitor. Then we introduced our chemiluminescent Oxides of Nitrogen instruments that operate with air at atmospheric pressure.

We were told that it would never work, but why has all our competition started advertising that their instruments have the same features?

If you really want proof we were first, you will be interested to know that REM has been issued U.S. Patent No. 3,710,107 entitled "Atmospheric Monitor by Means of Chemiluminescent Reaction."

REM Scientific is out front, and we intend to stay there. As you can see, we already have a family of instruments for air pollution monitoring, and we will be adding more all the time.

Demonstrated reliability is hard to beat. Repeat sales to customers who keep coming back are our best testimonials.



REM

SCIENTIFIC, INC.

Instrumentation for Environmental Technology

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