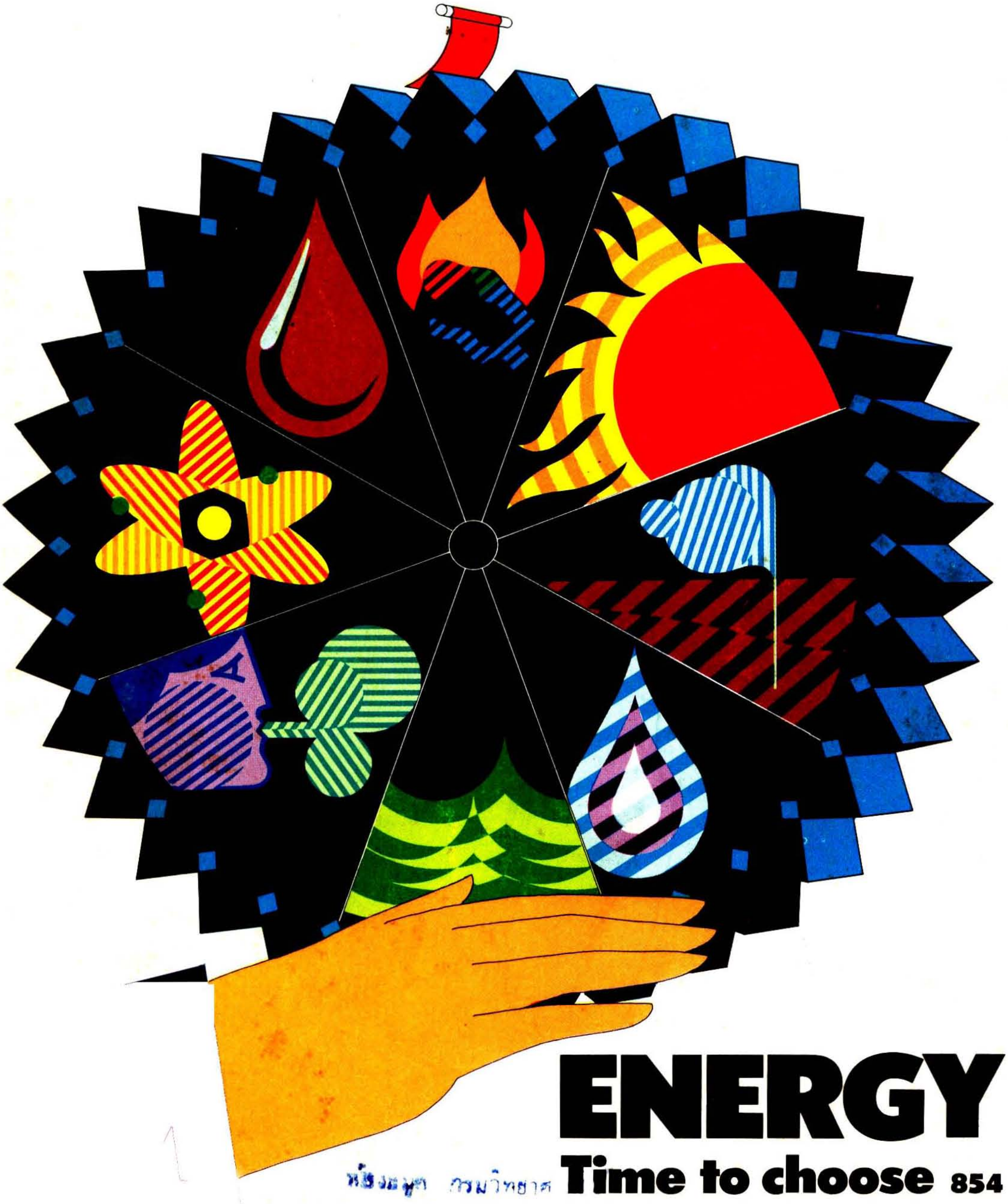
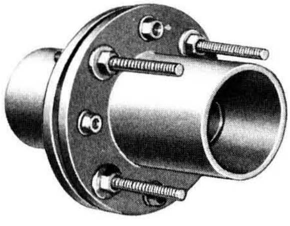
Environmental
Science & Technology

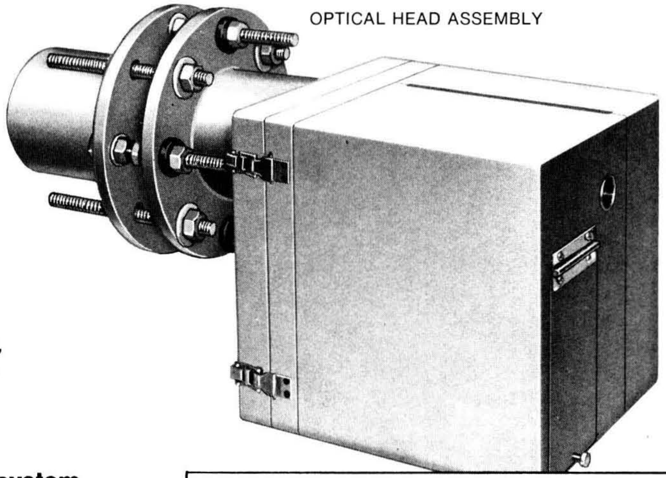
SEPTEMBER 1976



ENERGY
Time to choose 854

RAC on-stack transmissometer *

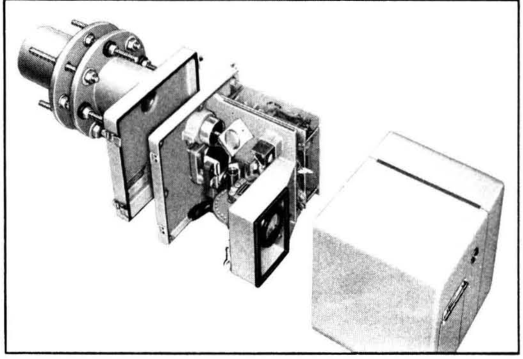


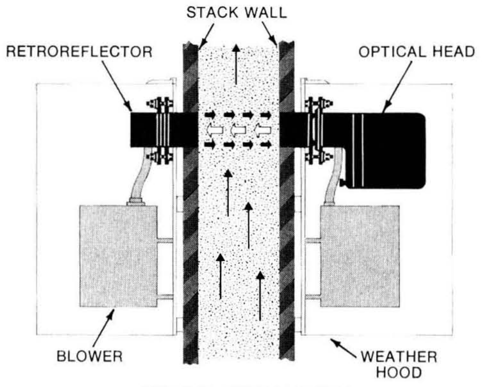


** Meets or exceeds all performance specifications outlined in the Federal Register, Vol. 40, No. 194, dated 10/6/75.*

This advanced electro-optical system measures from 0 to 100% opacity in stack gas streams . . . provides direct readouts with accuracy of ±3%.

The RAC on-stack transmissometer accurately measures stack gas stream opacity by means of a modulated light beam. A highly precise instrument, with patented design/operating features, this dual-beam monitoring device uses more simplified optic and electronic subsystems than competitive units. Its advanced design assures optimum optical performance . . . minimizes operating problems as well as normal service/maintenance requirements.





TYPICAL INSTALLATION

The RAC transmissometer features a unique chopper design and a solid-state automatic control circuit. These components make the system insensitive to ambient light, provide continuous recalibration (every 0.1 second), and automatically compensate for light and temperature changes as well as aging/drift in the electronics. In addition, the system's calibration can be verified easily, while the unit is operating, by a unique system response test kit with four NBS filters.

Once properly installed, this compact, lightweight (37 lbs) system normally requires no further on-stack adjustments. The optical head and retroreflector units, after fine alignment, are locked in position by external threaded connections to assure a vibration-free installation.

A variety of accessories—including blower units to protect the optics (when required), computer interfacing, remote strip-chart recorder, fail-safe shutter, remote control panel, linearizer-integrator, window soiling alarm, retro alignment tool, and a system response test kit with NBS filters—are available to enhance the RAC transmissometer's inherent capabilities for optimum performance with minimum attention.

STACK SAMPLING SEMINARS
Since 1970, RAC has sponsored an annual series of 2-day, technical, practical seminars on stack sampling parameters & procedures (EPA methods). **Write for descriptive folder.**

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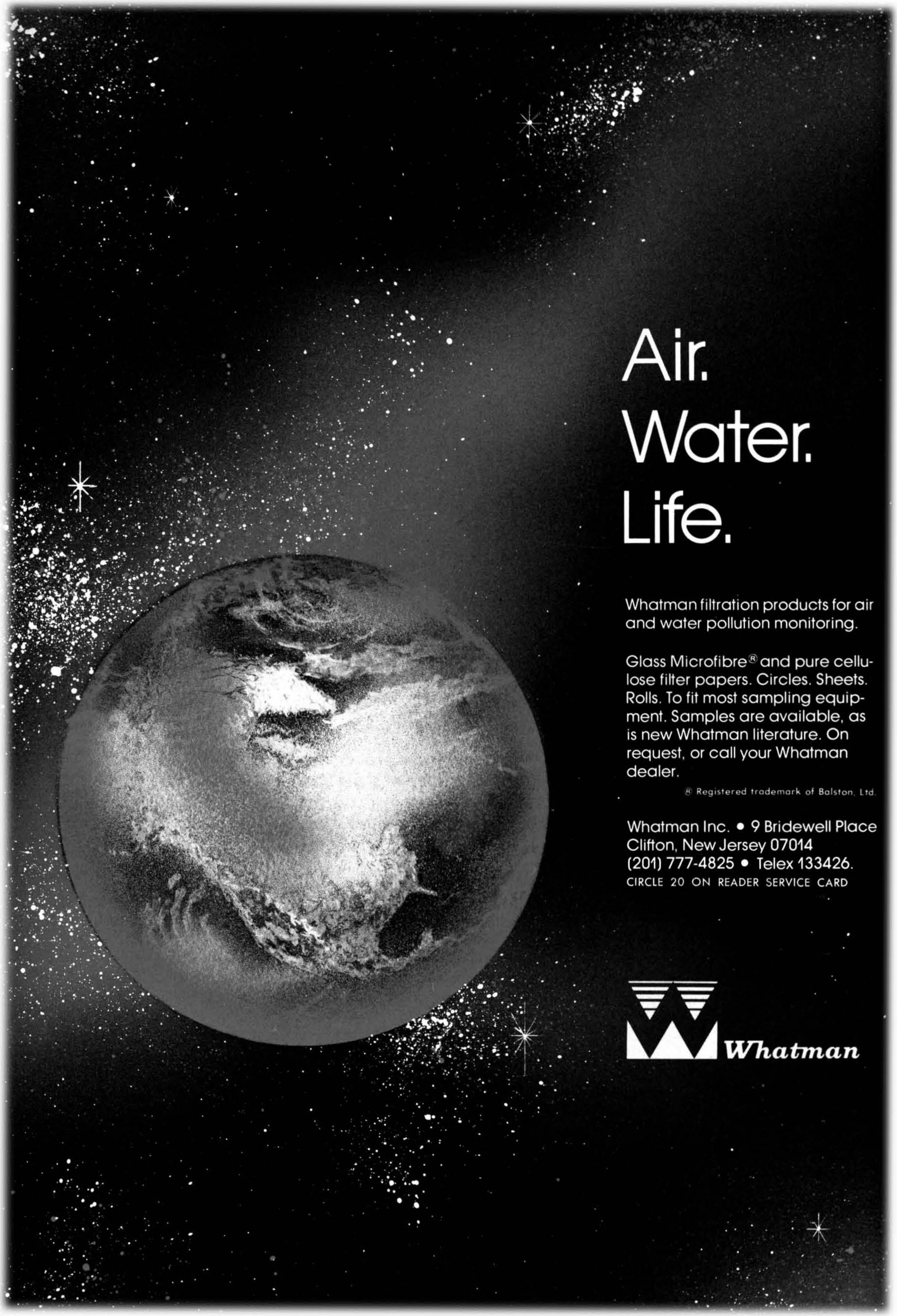
Technicon AutoAnalyzer II



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Volume 10, Number 9, September 1976

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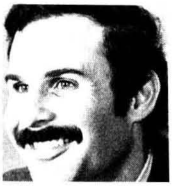
CONTENTS

862

872



849

Special report

PAT report

Features

Outlook

Departments

Current research

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CURRENT RESEARCH

Atomic absorption and optical emission analysis of NASN atmospheric particulate samples for lead **877**

D. R. Scott*, D. C. Hemphill, L. E. Holboke, S. J. Long, W. A. Loseke, L. J. Pranger, and R. J. Thompson

945 different particulate samples are analyzed for Pb by optical emission and/or atomic absorption spectroscopy. No difference between Pb content of different sections of the same filter is found. A difference of 8% is found between the two methods, the optical emission data being higher.

Decomposition of solid organic materials in the deep sea **880**

C. O. Wirsen* and H. W. Jannasch

Solid organic materials incubated deep at sea show less degradation than controls from shallow water. These data and the results of similar experiments indicate that no population of free-living microorganisms adapted to the deep sea exists.

Kinetic studies of sulfur dioxide absorption by manganese dioxide **886**

K. D. Kiang, Kun Li*, and R. R. Rothfus

A nontopochemical model is proposed for the kinetics of SO_2 absorption by pellets of MnO_2. The reaction is assumed to be irreversible, first order, and proportional to reacting surface area. Agreement between the model and experimental data is satisfactory.

Thin-layer chromatographic technique for identification of waterborne petroleum oils **893**

W. A. Saner* and G. E. Fitzgerald II

A TLC method for "fingerprinting" petroleum pollutants is developed. Compounds are extracted using acidified methanol and chromatographed on silica-gel plates. Detection is by UV fluorescence and iodine staining.

Comparison of ozone determinations by ultraviolet photometry and gas-phase titration **897**

W. B. DeMore* and M. Patapoff

Comparison of UV absorption spectrometry and gas-phase titration reference methods for O_3 determination shows good results. The gas-phase titration method is not recommended for calibration of O_3 monitors because of susceptibility to experimental errors.

Petroleum analysis: methodology for the quantitative and qualitative assessment of oil spill **900**

H. S. Hertz*, W. E. May, S. N. Chesler, and B. H. Gump

Headspace sampling, gas chromatography, and coupled-column liquid chromatography are used in quantitation of oil spill samples. GC–MS is used to identify individual components. Data from a major oil spill are presented.

Atmospheric particulate mass measurement with beta attenuation mass monitor **904**

E. S. Macias* and R. B. Husar

An aerosol mass monitor with size separator using a beta attenuation technique is developed. The instrument is controlled by a programmable calculator that also handles the data. Precision is 4 $\mu g/m^3$, and accuracy is 11%.

Ozone formation potential of organic compounds **908**

J. J. Bufalini*, T. A. Walter, and M. M. Bufalini

A reactivity scale for organic compounds based on O_3 formation is presented. On theoretical grounds it predicts that all hydrocarbons lead to O_3 formation, and larger molecules to more O_3. The scale predicts that high levels of O_3 will be found downwind from emission sources.

Determination of sulfur dioxide in stack gases by ultraviolet absorption spectrometry **913**

H. E. Winkler and Augusta Syty*

SO_2 is concentrated from stack gases by bubbling through a tetrachloromercurate solution. Reaction of the samples with H_2SO_4 generates SO_2 which is measured in an atomic absorption spectrometer at 210 nm. Sensitivity is to 3 mg SO_2/m^3 in air based on a 20-l. sample.

Sampling for contaminants in ecological systems **917**

L. L. Eberhardt*, R. O. Gilbert, H. L. Hollister, and J. M. Thomas

Sampling models of five classes are reviewed, and while a universal model is out of reach, present ones serve many purposes. Adaptation of an industrial experimentation method and techniques used in economic geology to ecological sampling is recommended.

Determination of vinyl chloride at the μg/l. level in water by gas chromatography **926**

T. A. Bellar*, J. J. Lichtenberg, and J. W. Eichelberger

Vinyl chloride in water is transferred to the gas phase by bubbling inert gas through the water. After concentration on silica gel or Carbosieve-B, determination is by GC. Confirmation of vinyl chloride is by GC–MS.

NOTES

Determination of micro-quantities of chrysotile asbestos by dye adsorption **930**

M. C. Markham* and Karen Wosczyna

Airborne asbestos is analyzed by differential dye adsorption. Quantities can be estimated down to 100 μg. For industrial use, asbestos samples must be separated from interfering minerals by density flotation.

Capture of Hg^{2+} ions from effluent stream by cellulose derivatives **931**

Francesco Gasparrini, Gianni Palmieri, Giovanna Cancelliere, Mauro Ghedini*, and Giuliano Dolcetti

Capture of Hg^{2+} from aqueous solutions by cellulose derivatives is tested. A system is proposed for Hg^{2+} ion removal by elution through a 10-undecylenate column, then elution through an *o*-aminothiophenol cellulose column.

CORRESPONDENCE

Evaluating Environmental Impacts of Stack Gas Desulfurization Processes **934**

T. F. Evans
Chiou-shuang Yan

Ozone Formation from NO_x in Clean Air **934**

B. Dimitriades, M. C. Dodge, J. J. Bufalini, K. L. Demerjian, and A. P. Altshuller
H. E. Jeffries and M. Saeger
W. L. Chameides and D. H. Stedman

*To whom correspondence should be addressed.

This issue contains no papers for which there is supplementary material in microform.

Credits: 849, EPA's Don Moran; 867, A. Rocco

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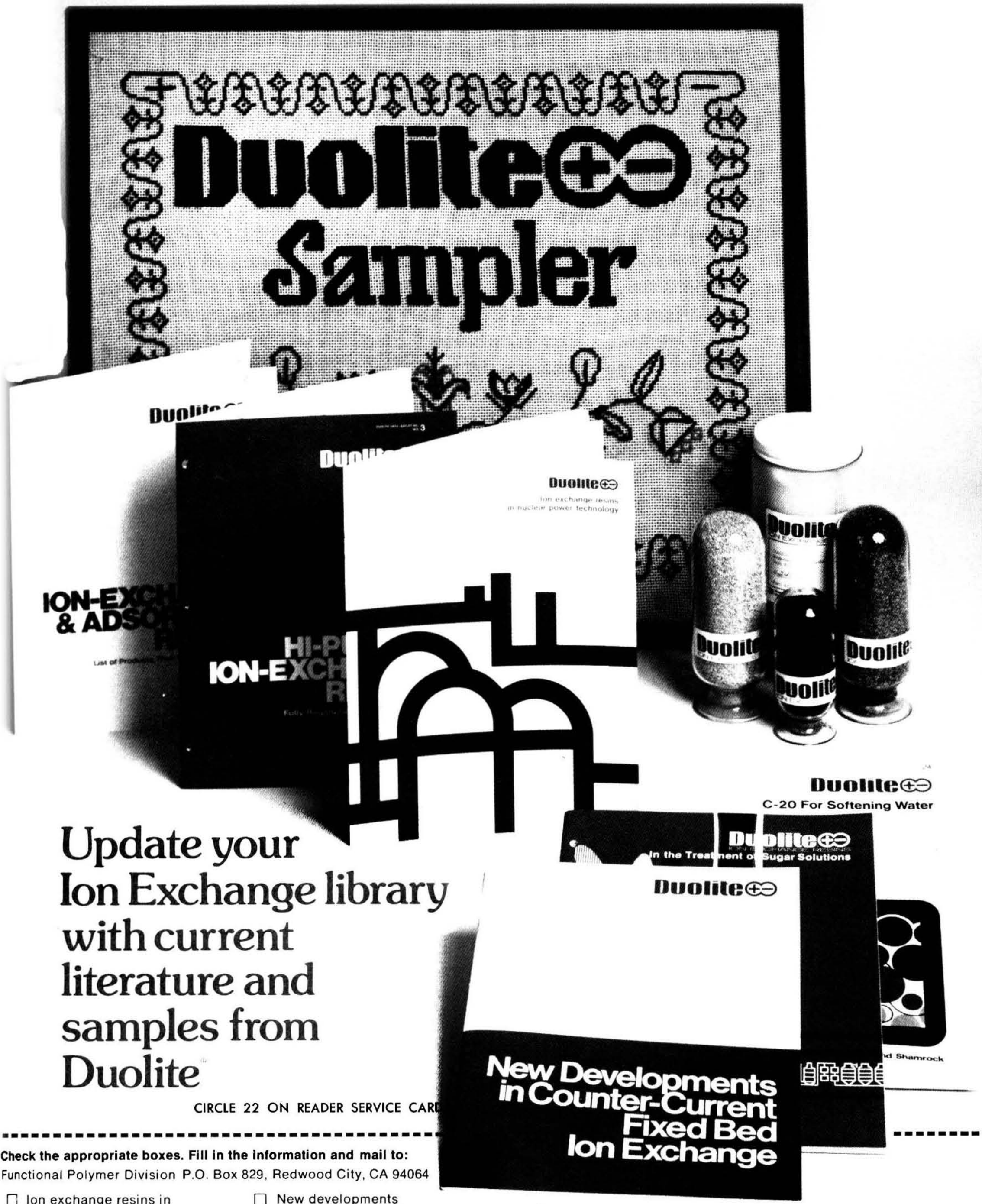
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Chloroform controversy

Indications are that the Environmental Defense Fund will bring suit against EPA over the latter's failure to regulate the concentration of chloroform in drinking water. At issue here is whether or not the Administrator of EPA has complied with the requirement of the Safe Drinking Water Act to set standards or require treatment for contaminants, which in his judgment, "... may have adverse effect on the health of persons."

What scientific basis does the Administrator have for determining that chloroform has an adverse human health effect? EPA's NORS survey has established that chloroform, and often other trihalomethanes, are present in virtually every chlorinated public drinking water. Data on the effect of chloroform on living systems are not extensive but are available for three species (rat, mouse, and dog) by two routes of exposure. In five studies a tumorigenic response has been noted, although in four studies no tumors were found. The National Cancer Institute found kidney epithelial tumors in male rats and a high frequency of hepatocellular carcinoma in mice of both sexes exposed to chloroform for a year and a half. Most importantly, both the incidence of tumor development and the latency period showed a dose-related response.

Differences in exposure levels and in metabolic pathways make extrapolation of these findings to man difficult but not impossible. Preliminary extrapolation by EPA scientists indicates that the risk to humans may be somewhere between zero and a maximum of 1.6 cancer deaths per million per year from the consumption of chloroform in drinking water. Available data and present experimental tools do not permit a more accurate description of the human risk at this time.

EPA has handled this matter in an open, scientific, and responsible manner. They have performed surveys of chloroform occurrence, sponsored and performed research on the mechanism of chloroform formation and removal, established health effects as a principal focus in their research budget, and have actively sought public discussion and comments on options for Agency action. As a result of the suit, however, lawyers may now decide whether the present scientific evidence defines a human health hazard. It will be unfortunate if their decision forecloses the available option of waiting for more adequate scientific data.

R F Christman

The Calgon Adsorption Service.℠

It controls organic pollution and recovers materials worth real dollars.

Carbon adsorption of dissolved organic materials from wastewater (including toxic and refractory compounds) is one of the most cost-effective methods now available. Calgon has packaged its carbon adsorption expertise into compact, modular treatment units that we install, maintain, and can even operate on your property for a preagreed-on service fee. No major capital investment for you. We can be operating in as little as 45 days after the service agreement is completed.

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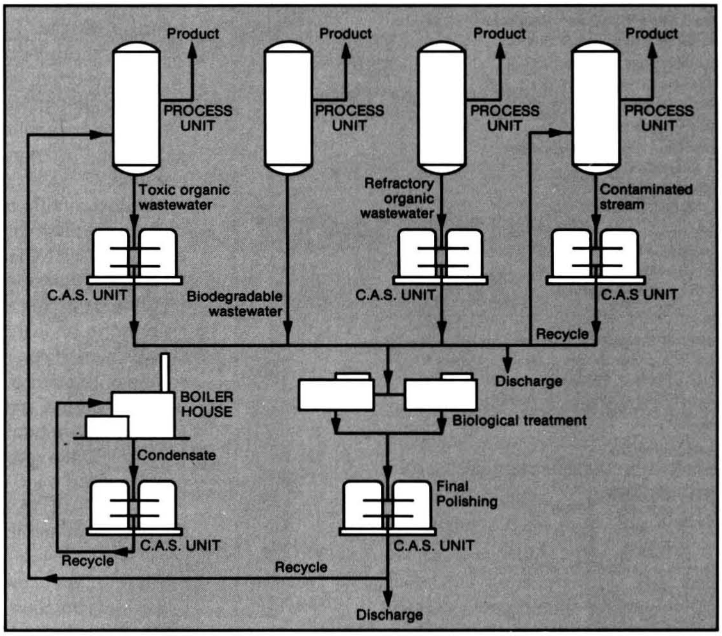
PRODUCT RECOVERY—There's often enough valuable organic material in a wastewater stream to justify recovery for return to the process. Calgon Adsorption Service systems concentrate the organics in the granular carbon from which they can be recovered. Alternatively, contaminated product streams can be processed for removal of contaminant so the product stream can be recovered.



IMPROVED BIO SYSTEM OPERATION—By reducing the concentration of organic materials—some of which may be toxic to the biomass—in a waste stream before it goes to an existing biological treatment unit, a Calgon Adsorption Service system can increase efficiency greatly. The adsorption system also can be used to upgrade the effluent from a biological plant.

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(201) 526-4646 in Bridgewater, New Jersey.

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Furthermore, at the Congress, you'll be able to listen to and talk with the people who have responsibility for implementing and complying with these tough laws.

And because much of this legislation is being adopted by other areas, we expect thousands of attendees from all over the country. People anxious to find practical solutions to present and future problems.

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Philips SO_2 monitors: 90 days, 90%... 90 years?

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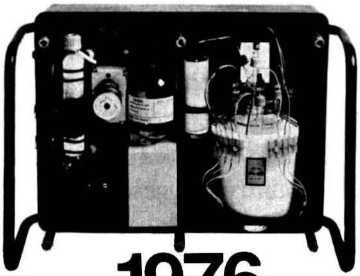
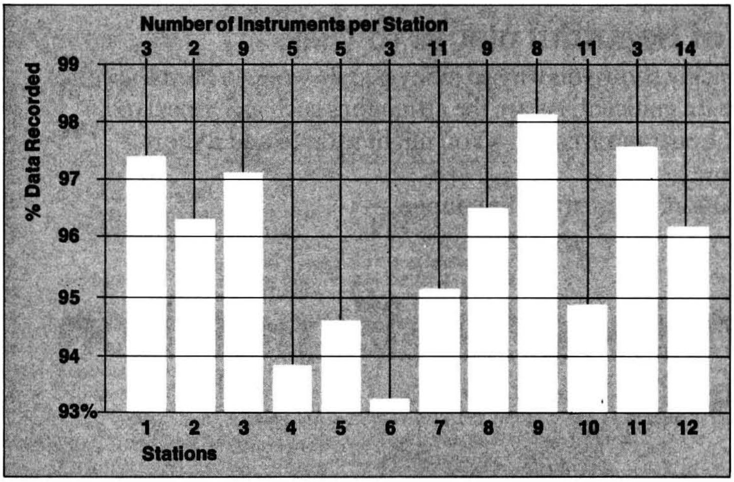


1976

. . . over 60,000 data hours later this Philips SO_2 monitor is still on duty, still producing 90-95% *valid* data on an annual basis.



High quality means high performance: *95.9% average recovered data from a 12 station 83 monitor system. Record covers a 10 month period. The data above was validated by a multi-point external calibration using the following schedule: 24 hours, 7 days, 45 days.*

This is why . . .

Philips designed the monitor around a 90 day scheduled maintenance program

90 day unattended operation, together with 90 day scheduled maintenance establishes the basis for Philips unequalled field performance and for its broad acceptance. Implied by these tough field performance criteria are design standards of the highest level. Today, seven years after the introduction of the PW9700 SO_2 monitor, Philips remains the *only* manufacturer to offer 90 day standards for unattended operation and for scheduled maintenance—no one else is even close.

Design criteria that make the 90 day scheduled maintenance program possible include . . .

Highest quality components. Components selected for the monitor must pass a quality assurance program to satisfy the necessary MTBF for 90 day unattended operation. Success of this program is attested by the more than 2500 monitors now in the field worldwide and routinely reporting a 90% or better data recovery.

Automatic regeneration of reagent. A constant level coulometric cell with automatic regeneration of reagent provides for a 6 month life of the electrolyte.

Philips designed the monitor around a built-in data quality program

Continuous data validation. Automatic, daily systems zero* and dynamic span† checks are made

---

*An activated charcoal filter incorporated in the monitor provides a pure air sample to generate a system zero signal.

†In the PW9755 a thermostatted SO_2 permeation source, traceable to an NBS standard, is used to provide a known amount of SO_2 when a calibration command is received.

to assure continuously validated information from the monitor.

Philips monitors get off to a good start

The Philips monitor is installed and made operational at the customer's facility by a Philips service engineer. The instrument is released to the customer only after the system has been verified as meeting specifications. This service is provided to the customer as part of the purchase price.

Philips nationwide service organization assures prompt local support

Our 12 month field warranty brings prompt on-site service to the customer as required . . . and at no cost to the customer.

Philips highly trained service engineers operate from 14 service offices throughout the nation. On-going schooling programs for these engineers assure up to the minute competence in their performance.

Philips support assures continuing performance

At the time the equivalency document was published, our PW9700 SO_2 monitor had been superseded by the PW9755 (see below) and was no longer in production . . . Philips, nevertheless, embarked on a program, prior to the promulgation of the document, to bring the PW9700 in line with future requirements, and filed for equivalency on behalf of this instrument.

Philips listens to its customers

After extensive field experience and component design improvement programs, Philips, in 1976, introduced an updated version of the PW9700, the PW9755—even though the older model still has no peer for field performance.

1981

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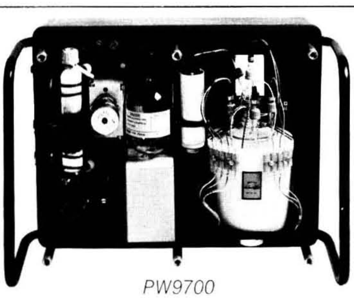

PW9700

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LETTERS

Dredging

Dear Sir: The April issue of *ES&T* contained three articles (pp 326–338) on dredged material regulation and research. In view of the National Wildlife Federation's considerable interest in this subject, we are moved to offer the following comments.

The articles by Lee and Smith point up one of the biggest problems in disposing of dredged material in a way that satisfies legal requirements and environmental protection concerns. As Lee indicates, "what is needed is a procedure by which the potential significance of chemical contaminants in dredged sediments can be assessed *prior to* dredged material disposal." Implications for both water quality and ecological and biological integrity need to be evaluated.

Yet, the existing EPA guidelines under section 404 of P.L. 92-500 and the ocean dumping criteria under P.L. 92-532 fall far short of prescribing procedures for assuring that these environmental implications are addressed, much less addressed adequately. Thus, an "elutriate" test is provided for which, at most, tells one how much of various "major constituents" will be released from the dredge spoil into the water column over the relatively short term. As Smith notes, "benthic species can ingest contaminated sediment particles," and can become contaminated or poisoned without any escape of major constituents into the water at all. Furthermore, it is now well known that certain heavy metals (e.g., mercury, arsenic, lead, selenium, and tin) can be methylated into more soluble and more toxic forms in the environment as a result of biological activity. Such transformations would never be detected in any elutriate analysis. To add insult to injury, dredged or fill material may be excluded from even elutriate procedures if certain less-exacting qualitative requirements have been met.

To be sure, the kinds of bioassay and other characterization procedures necessary to adequately evaluate environmental consequences of dredge disposal often lie near the limits of the present state-of-the-art. However, there are "worst-case" assumptions that can be made to assure necessary protection to the environment. When the state-of-the-art improves, case-by-case evaluations may be more reliable and disposal restrictions can perhaps be lightened. The reverse approach—of applying loose restrictions until and unless state-of-the-art improvements indicate otherwise—will not protect the environment and is contrary to the law of the land.

We cannot agree with Lee that more field studies are the answer, at least for the foreseeable future. As was noted recently by a British scientist (*New Scientist,* April 29, 1976, pp 219–221): "Present survey strategies appear to be based on such inadequate theoretical frameworks that they cannot possibly interpret subtle environmental changes. An understanding of these effects will require detailed study of biological interactions over many years. Short-term, on-off "impact" statements or "base-line surveys" cannot be expected to provide an adequate framework for monitoring environmental changes."

We'd prefer to place our trust for the interim in laboratory and *in situ* bioassays, coupled with a healthy dash of respect for basic ecological principles.

Kenneth S. Kamlet, Counsel
National Wildlife Federation
Washington, D.C. 20036

Groundwater

Dear Sir: I read with much interest and great disappointment the article "Quality Assurance for Groundwater" (*ES&T,* March 1976, p 226).

My interest in groundwater protection parallels much of what was expressed throughout the first half of the article. Certainly, groundwaters that lend themselves for public use need to be protected from pollutants and contaminants that may threaten human health. However, in the latter half of the article mention is made of human and animal wastes, and enteric viruses from human wastes being detected in groundwater supplies. Additionally, it was noted that "the major source of these viruses turned out to be leachates from *sanitary* landfills in which many disposable diapers containing untreated fecal matter had been buried".

There is much confusion and misunderstanding regarding land disposal sites. Unfortunately, many individuals fail to distinguish among the types of waste disposal sites—for example, dump, covered landfills, and engineered sanitary landfills. My disappointment and alarm stems from the fact that the author himself or the spokesman from the EPA Office of Water Supply implies that the disposable diapers containing untreated fecal matter gave rise to enteric viruses that resulted from leachates generated in a sanitary landfill site—with emphasis on the term "sanitary". I question whether the site was indeed a sanitary landfill site or whether it was an improperly operated waste disposal site. In the absence of clarification and with the emphasis on "sanitary" it almost seems as if the author is taking a "cheap shot" at sanitary landfilling—a necessary approach for effectively managing our discards.

NSWMA as the professional trade association for the solid waste management industry has strongly supported sanitary landfill as an environmentally acceptable method of waste disposal. Therefore, it is imperative that those proficient in this field clearly differentiate between what constitutes a sanitary landfill versus an open dump.

James R. Greco
National Solid Wastes Management Assn.
Washington, D.C. 20036

Opacity

Dear Sir: We were appalled by the feature article, "Factors Influencing Plume Opacity" (*ES&T*, June 1976, p 539). We did not realize that scientific facts could be juxtaposed in such a way to so thoroughly misrepresent the true situation. This article attempts to show that the use of visual opacity observations by control agencies for quantitation of particulate emissions is an invalid technique. We fail to grasp the purpose of the article because, in our opinion, no responsible control agency, certainly not the Texas Air Control Board, would attempt to enforce a mass emission regulation by such means.

We have researched most of the available literature relating opacity and particulate concentration, and have yet to see a technique proposed that involves dependence upon human observers. Considerable field work has been performed in both Europe and the U.S. relating in situ opacity by transmissometer to particulate concentration. Good correlations have been established for cement plants, lignite-fired boilers, and other source types.

The article appears to be directed toward visual observers. Yet as a starting point the authors use the EPA work with transmissometers on opacity/mass correlations for an asphalt concrete plant. They extrapolate from this study to find a "black dot" equivalent opacity for power plants. Anybody who is at all expert in the field knows that mass correlation with opacity must be done on a process by process basis. The authors are mistaken in their assumption that opacity mass data for an asphalt concrete plant can be extrapolated to a predicted opacity for a coal-fired power plant at a similar concentration. Generally, correlations must be established for each individual source, the validity of the correlation dependent on process variables and degree of emission control. A highly controlled continuous process is likely to have particle characteristics sufficiently stable to permit mass determination by transmissometry. New Source Performance Standards requiring more efficient particulate control devices will expand the range and number of sources to which an opacity/mass correlation may apply.

Enforcing mass emission standards with opacity measurements is *not* difficult to justify on a technical basis as the authors claim, providing a method is chosen incorporating the best available technology applied with a full consideration of source characteristics that may bias the results. At worst, such a technique will provide a continuous indication of mass emission rate at nominal additional expense where opacity monitoring requirements already exist.

We must also take exception to the authors' implications regarding the inability of trained observers to accurately assess plume opacity. An EPA contract study by Southwest Research Institute (Hamil, et al. ref. 2) has verified the accuracy of visual observations on three types of sources with an accuracy greater than that specified in Method 9. They also neglected to mention that Connor's work was used as the basis of establishing opacity observer procedures so that observations will tend to be *low.* This is verified in the Hamil study and confirms our own investigation of our agency's visual observer certifications. As for the "problem" of uncombined water, it is a simple matter for trained observers to determine the point in the plume at which water ceases to be a factor in the opacity and evaluate it at that point. This technique, while perhaps not "scientific" in the sense that the authors are seeking, has produced good results in Texas.

Visual observation of plume opacity serves most importantly as a rapid indication of source operational status and as a control on highly visible submicron particles that may pose the most serious health hazard. The enforcement of visual standards serves in an aesthetic capacity as well, by maintaining visibility in the community. For this reason, a control agency concerned with the appearance and visibility of a plume will choose to regulate the worst case without regard to time of day, season, or geographic location, providing that proper observation conditions are met.

Finally, the authors reference Haythorne and Rankin. Haythorne and Rankin either did not read their own references, did not understand what they read, or deliberately misrepresented those references. They speak of observers reading consistently and grossly high on plumes. Yet when the references are checked, it is found that those observations were individual observations, not an average of 20–25 readings, and the observers were deliberately placed in the worst observing positions. This is only one example of several misrepresentations in the Haythorne article.

The only point of possible value in this whole article is the effect of geographic location. However, since these appear to be calculated numbers and not actually observed, we have some serious doubts. Because their "black dot" point is an extrapolation from a different process (not valid) and no experimental evidence is given, any calculations are questionable. Finally, if that "theoretical" plant were in Texas, whether the opacity was 50% or 85% it would still be a violation.

The authors' time might better be spent evaluating the most likely opacity/mass emission correlation method—the optical transmissometer and variations thereof—rather than laying to rest a technique that should not be considered as a serious option. Some additional reading that may be helpful to them is listed.

(1) Pilat, M. J., and Ensor, D. S., "Plume Quality and Particulate Mass Concentrations," *Atmos. Environ.*, V.4N.2 pp 163–173 (1970).

(2) Hamil, H. F., et al., "Evaluation and Collaborative Study of Method for Visual Determination of Opacity of Emissions from Stationary Sources," EPA-650/4-75-009 (1975).

(3) Reisman, E., et al., "In-Stack Transmissometer Measurement of Particulate Opacity and Mass Concentration," EPA-650/2-74-120 (1974).

(4) Beutner, H. P., Measurement of Opacity and Particulate Emissions with the Lear Siegler On-Stack Transmissometer, No. 73-169, 66th Annual Meeting of the APCA, June 24, 1973. (Note: Last half of paper deals with various processes.)

(5) Hood, K. T., and Coron, A. L., "The Relationship Between Mass Emission Rate and Observed Plume Appearances From Kraft Recovery Furnaces, 74-AP-08, Regional APCA Meeting, Boise, Idaho, November 17, 1974.

(6) Duvel, L., Etudes Comparées Des Différentes Principes De Mesures Utilisés Pour Les Contrôles Permanents Des Poussières Emises Par Les Chaudières Chauffées Au Lignite (available in English), CPO19F, Second International Clean Air Congress of the International Union of Air Pollution Prevention Association, December 6, 1970, Washington, D.C.

C. Dean Wolbach, John W. Key
Source Evaluation Section
Texas Air Control Board
Austin, Texas 78758

Opacity

Dear Sir: Reference is made to factors influencing plune opacity (*ES&T*, June 1976, p 539). Although I am in sympathy with the argument and views of the authors, I feel it is necessary to comment on the claim that the effects of uncontrollable factors were 'previously unrecognized.' I would like to draw the authors attention to the work of R. T. Jarman & C. M. DeTurville of the CEGB in the U.K. In their 1969 paper on the Visibility and Length of Chimney Plumes (*Atmos. Environ.*, 1969, Vol. **3**, pp 257–280) Jarman and DeTurville extended Nonhebels theoretical analysis to incorporate the scattering of sunlight and skylight by plume particles. The work of Jarman and DeTurville on plume persistence is relatively well known in the U.K. and I would like to recommend it to those studying these phenomena.

D. E. Shillito
Cremer and Warner
London, SW1W 9SQ

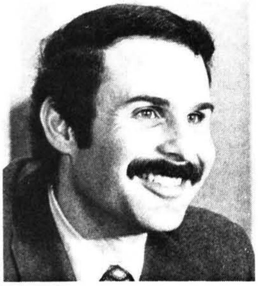
CURRENTS

INTERNATIONAL

Japan's NO_2 standard, 0.02 ppm/24 h, is too stringent, Dr. Raisaku Kiyoura of the Research Institute of Environmental Science, told participants at the Air Pollution Control Association's recent conference. In his remarks he stated that Japan's air pollution and population density do not warrant this low level, which is 5–7 times more rigid than any other country in the world. He also stated that "the procedures adopted in the epidemiological and statistical studies . . . were proved to be unreliable and invalid by many scientists at home and abroad." Among the U.S. scientists cited were Dr. C. M. Shy, director, Institute of Environmental Studies at University of North Carolina and Dr. V. A. Newell, director, Research and Environmental Health Division, Exxon Corp.

WASHINGTON

EPA is gearing up to revise and update the air quality criteria documents that form the scientific and legal basis for the federal ambient air quality standards. Roger Strelow and Wilson K. Talley, assistant administrators for air and waste management and research and development, respectively, have instructed their staffs to develop a schedule for revising the six documents. This action was a recommendation of EPA's National Air Quality Criteria Advisory Committee (NAQCAC), which ceased to exist on June 30. The NAQCAC also recommended that a combined document for sulfur oxides and associated particulates and a separate document for particulate matter be developed. It also suggested combining the criteria documents for oxidants and hydrocarbons.


EPA's Strelow

EPA launched a program to control the discharge of 65 hazardous chemicals into the nation's waterways. These strict controls will be implemented by 1983 and will regulate such substances as arsenic, asbestos, cadmium, chloroform, lead, mercury, and vinyl chloride. Studies to assess the best available technology and the economic implications of their implementation will begin soon. Based on the studies' findings, EPA will set maximum pollutant discharge standards by 1979 for at least 21 major categories of industries. For six highly toxic substances, including DDT, benzidine, and PCBs, EPA has already issued proposed regulations. EPA has called for comments from the public on ways to control organic chemicals in drinking water, and has issued regulations to limit radioactivity in drinking water supplies.

OSHA has published inflation impact statements for a noise exposure and an inorganic arsenic regulation. OSHA estimates the annual compliance cost for the arsenic standard at $110.8 million, with the highest costs occurring in the copper smelting and wood preservation industries. At worse, about 3000 jobs would be lost nationwide. For the noise standard, OSHA estimates noise monitoring costs at about $155 million annually, and audiometric testing costs at $86 million. The Occupational Safety and Health Administration has recently issued voluntary guidelines, not enforceable as law, for airborne crystalline silica, lead, and mercury. OSHA is developing complete standards for these substances.

ERDA has published Volume 2: Program Implementation of its second annual National Plan for Energy Research, Development and Demonstration (ERDA 76-1). For each program listed, ERDA states both near-term (to 1985) and long-term (to 2000) objectives; describes technical, socioeconomic and environmental problems; and outlines its strategy for meeting each activity's objectives. The Energy Research and Development Administration has also issued its five-volume Final Environmental Impact Statement for the Light Water Breeder Reactor Program (ERDA-1541).

A government report finds the federal effort to protect the public from cancer-causing chemicals ineffectual. The General Accounting Office study states that the agencies have the legislative authority to regulate the hazardous chemicals, but they lack the scientific wherewithal to extrapolate animal safety tests to humans. The report states that the director of the National Cancer Institute has the responsibility to oversee the federal effort and should establish, with the cooperation of other agencies, a national policy on carcinogens. At the very least, this policy should include the data needed to regulate the chemicals, enumerate the chemicals to be tested in animals, and describe how the tests should be conducted and the results analyzed.

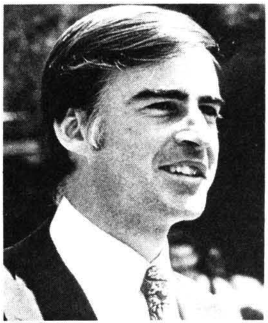
STATES

Big Chief Trucking Co. of Fort Lauderdale, Fla., was found guilty of violating a provision of the Clean Air Act. This is the first time a company has been found in violation of the hazardous air pollutant provision of the act. EPA took Big Chief to court after citing it for failure to remove asbestos-insulating materials in dust-tight containers from a New Orleans wrecking site. On July 14, the judge, sitting in the U.S. District Court for New Orleans, fined the company $25 000 and the supervisor on the job $1000, and placed both on 5-yr probations.

Five states and the District of Columbia were notified that their clean air State Implementation Plans must be revised. The SIPs of Del., Md., Pa., Va., W.Va., and the District of Columbia were found inadequate to attain and maintain ambient standards for certain pollutants in certain areas. The entire EPA Region III was found to require more stringent controls on hydrocarbons. The Washington, D.C., Baltimore, and Philadelphia metropolitan areas, and the southwest

Pa. area were found to need better carbon monoxide controls. The areas cited for better particulate matter control were Pa., Washington, D.C., the Baltimore metropolitan area, the Cumberland, Md.-Keyser, W.Va. area and several areas in W.Va. Better sulfur dioxide controls were found to be needed in the southwest Pa. area. For the U.S., a total of 45 states were advised that they had to revise their SIPs.

California's Gov. Brown signed into law a measure that creates the South Coast Air Quality Management District to coordinate air pollution control efforts throughout Los Angeles, Orange, Riverside, and San Bernardino Counties. The measures creates a 10-member governing board, requires this board to develop and implement a comprehensive smog abatement program, permits this new district to establish fees for variances and penalties for violations of emissions standards, and creates an Office of Small Business Assistance to help small businesses meet air pollution regulations. The Air Resources Board plans to resubmit a proposal to the California legislature that will control SO_2 emissions in the South Coast Air Basin through a system of emissions charges rather than a regulatory scheme.


California governor Brown

Connecticut's Dept. of Health adopts new drinking water standards effective June 1, 1977, except for the color standard, which goes into effect June 1, 1979. Every water utility must conduct a survey of the watershed under its control, and report the results yearly to the department. Bacteriological tests for coliform organisms and physical tests for color and turbidity must be conducted quarterly. Tests for chemicals such as arsenic, cadmium, and mercury, and for chlorinated hydrocarbon and chlorophenoxy pesticides must be conducted annually. Facility siting requirements and radioactivity levels in water are also specified. On the other hand, Pa. and Ind. were listed by EPA as the only states that have not applied for grant funds allocated for their use to establish and administer a safe drinking water program.

Levels of carbon monoxide in New Jersey's air have declined an average of 14% since the inception of auto exhaust emissions inspections in 1974. Gasoline consumption, on the other hand, has begun to climb back to its pre-1974 levels. Recorded health standard violations in 1975 were 60% fewer than in 1973. These statistics were reported in "New Jersey Motor Vehicle Emission Inspection Program Summary and Report—Phase I." On the water front, N.J.'s Dept. of Environmental Protection plans to award a $1.05 million contract to a consortium of five companies for the preparation of the state's first statewide water supply master plan.

New Orleans recently dedicated a full-scale system to recover marketable materials from municipal solid wastes. This $6.5 million plant, the nation's first such facility, will initially shred 650 tons/day of refuse that will be disposed of in an environmentally controlled landfill. After the addition of materials recovery equipment, by early 1977, the second phase will begin by recovering steel, non-ferrous metals, glass, and paper from the waste. This facility, Recovery I, replaces three municipal incinerators that no longer meet environmental standards. Processing costs are estimated at $10.95/ton. It has been estimated that more than 1200 tons of steel, 1200 tons of glass, 94 tons of aluminum and 520 tons of paper could be recovered each month.

MONITORING

How do air pollution plumes affect regional weather? To find microscopic links between weather and pollution from stationary and mobile sources, NOAA (Boulder, Colo.) is flying a "Sniffer"—¼ ton of delicate sensors—into these plumes. The object is to measure physical and chemical processes as they occur in air pollution plumes, and to learn how pollutants evolve chemically after they enter the atmosphere. Also being sought is knowledge of how these pollutants modify weather, especially precipitation, downwind of their source, and how a pollutant source in one location can diminish air quality in communities scores of miles away. It has already been found that effects of pollutants from apparently similar sources vary greatly from place to place.

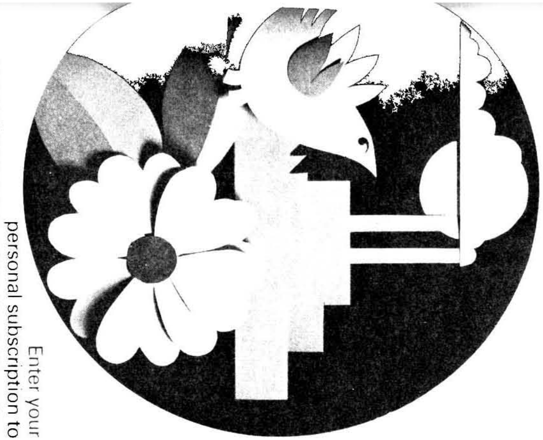
TECHNOLOGY

Conversion of high-sulfur coal to clean pipeline-quality gas received a boost when ERDA's HYGAS plant, operated by the Institute of Gas Technology (Chicago), gasified 640 tons of high-sulfur, caking Illinois bituminous coal on a self-sustained basis for 9 days. "Self-sustained" means that the plant made gas from steam, oxygen, and coal with no supplemental hydrogen and heat sources. Coal feed reached 3 tph. Caking was prevented by pretreating coal at 800 °F prior to feeding into the reactor vessel. Hydrogen and coal were reacted in fluidized beds at high temperatures and pressures to produce gas. The necessary heat and hydrogen came from reacting steam, oxygen, and residual coal char; that reaction allowed the system to be self-sustaining.

To reduce the volume and moisture content of clarification sludge so that it can be economically hauled to fill areas, and not use up fill areas too fast, one approach is a clay-polymer clarification program. According to Nalco Chemical Co., the trick is to use finely divided clay to add artificial turbidity to wastewater, and then to use cationic polymers—which work best in high turbidity. The clay is then coagulated along with the water's original turbidity and, according to Nalco, a rapid-setting "floc" and excellent supernatant clarity result. The technique, tried at Birmingham, Ala., is supposed to be easier than filter press dewatering of alum sludge, quickly set up, and not needful of any capital investment.

One of the world's largest all-fiberglass industrial air pollution control systems has been completed and shipped by Century Industrial Products (CIP, Irvine, Calif.). The system, known as a Low Energy Wet Scrubber (LEWS) needs only 120 hp to run water pumps and fans to remove particulates and dust from 100 000 cfm hot, dust-laden gases. The dust is removed by minute water droplets and forms a non-toxic sludge that can be reprocessed or landfilled. The LEWS uses 1.2 mgd of water, but recycles about 97.5% of it. The fiberglass construction provides high corrosion resistance, according to CIP. The LEWS will control dust from a 32-tph clay dryer at Southern Clay, Inc. (Bloomfield, Mich.), a maker of moisture-absorbent products.

Sulfate particles produced in automobile catalytic converters may disperse into the air, rather than remain concentrated near the ground, even on the worst days of calm with temperature inversion. This view was



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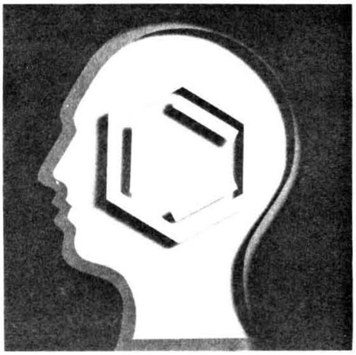

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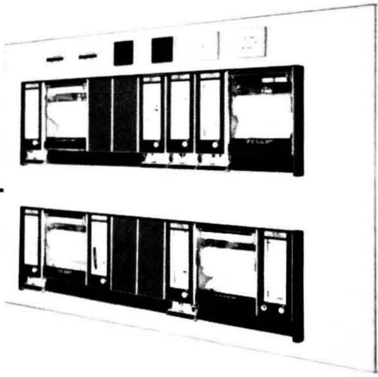

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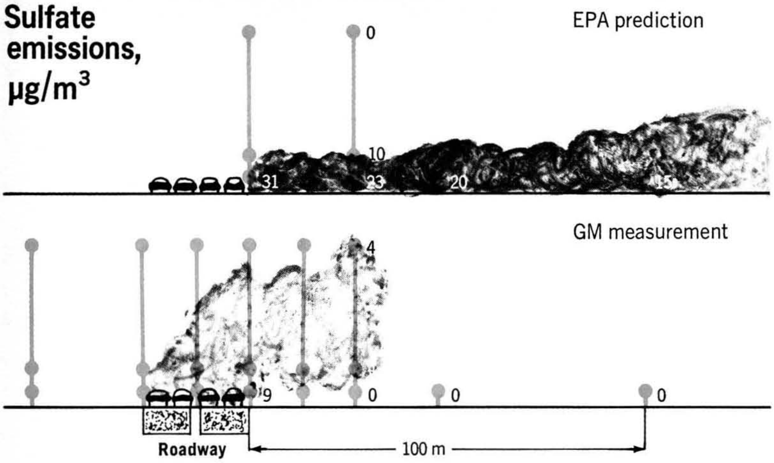


expressed by General Motors (GM) after extensive tests at its Milford, Mich., proving ground, and is at variance with EPA's model, which predicts heavy sulfate concentrations near the ground. Test results, according to GM, show that EPA's model "fails completely under the worst meteorological conditions." The company said that EPA's model did not account for effects of vehicle and exhaust gas turbulence, which would cause sulfates to mix efficiently with air in the vertical direction. GM also said that any health hazard level of sulfates is "highly speculative at the moment."

It may now be possible to separate plastics from municipal wastes according to the type of plastic, with each plastic type going to a different bin. According to a U.S. Patent issued to Arnold Horowitz of Scarsdale, N.Y., in July, a combination of electrostatics and radio frequency causes plastic particles of varying composition to be differentially heated in accordance with their respective dielectric constants and loss factors, with the result that they fall off a drum or belt at differently spaced intervals. Horowitz calculates that his plastics recovery system would cost less than 1¢/lb, and that certain recycled plastics for tarpaulins, pool liners, and other uses can sell for about 15¢/lb. He points out that new plastics cost about 30–35¢/lb to put on the market.

The chlorofluorocarbon-ozone layer depletion controversy heated up anew when Mario Molina of the University of California (Irvine) told a National Bureau of Standards press briefing that the formation of chlorine nitrate ($ClONO_2$) has little effect on ozone depletion, and that original predictions were correct. $ClONO_2$ is formed, apparently, when chlorine combines with NO_x, also an ozone destroyer. Experimental data, which raised hopes that $ClONO_2$ formation materially reduced the ozone depletion threat, turned out to be in error. Also, Molina said that what $ClONO_2$ is formed occurs at 25–30 km altitude—not at 35–40 km where it would really help. Meanwhile, J. Peter Jesson of Du Pont said that the probable less than 20-yr lifetime of the fluorocarbons could cut ozone depletion predictions by 80%.

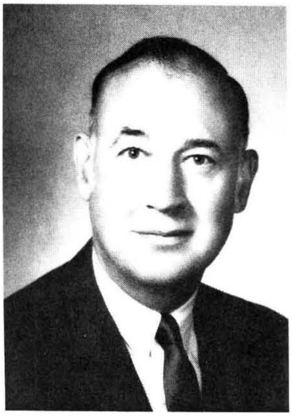
INDUSTRY

The Potomac Edison Power Co. (PEPCO, Washington, D.C.) has run into static concerning its plans to build a nuclear power plant at Douglas Point, Md. Plans were to build two reactors for startup in 1980 and 1982 (now delayed to 1985 and 1987), respectively, and would provide up to 56% of PEPCO's output. Two 400-ft high cooling towers would be included. Opponents of the project note that Douglas Point is in the heart of striped bass spawning grounds, and fear severe damage to the bass and other life. They also are apprehensive about the use of chlorine in the cooling towers, and its release to the Potomac River, as well as possible radioactive contamination. However, PEPCO's consultants say that the fish loss would come to only 0.6–1.7% of the total in the proposed site area.

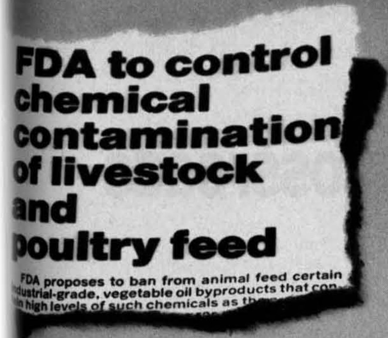
The American National Standards Institute (ANSI, New York, N.Y.) has launched a product to expedite development of standards most needed for noise control and abatement. The project was undertaken in coordination with EPA and OSHA. The ANSI panel directing the project will identify noise standards most urgently needed, and, where a need exists, identify the standards developing organization(s) most capable of carrying out the task. Another ANSI group is at work on a special effort to meet needs for standards for solar heating and cooling equipment (this issue, p 857), which the Solar Energy Industries Association hopes to see as a basis for tax "breaks" for installation of solar heating/cooling equipment.

The American Petroleum Institute (API, Washington, D.C.) warned the EPA and Federal Energy Administration that requiring too great a lead reduction too quickly is "virtually certain" to cause spot shortages of gasoline by next summer. API president Frank Ikard pointed out that lead "stretches" gasoline, and that lead reduction cuts the number of gal of "gas" that can be made from a bbl of crude oil. He also noted that refineries have been running near capacity, and have met "gas" demand by drawing on primary inventories over the past several months. He said that there may not be enough refinery capacity to meet demand for low-lead "gas" if EPA moves precipitately.

Reynolds Aluminum Recycling Co. paid $13 million for 86 million pounds of scrap aluminum last year. Company president Harold L. Albrecht says, "each time aluminum is recycled, it saves 95% of the energy required to make primary aluminum." All told, Reynolds has 72 permanent recycling plants plus 125 mobile units operating in 45 states. The scrap aluminum is recovered at the company's two smelting facilities (Richmond, Va., and Florence, Ala.). At present, the company pays 15¢/lb of scrap aluminum. Reynolds Aluminum Recycling Co., is a subsidiary of Reynolds Metals Co., the second largest aluminum company but first in the reclamation field (*ES&T*, November 1969, p 1157).

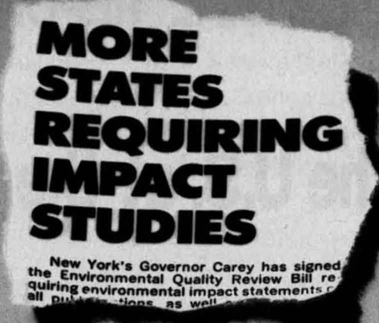


Reynolds' Albrecht


FDA to control chemical contamination of livestock and poultry feed

FDA proposes to ban from animal feed certain dustrial-grade, vegetable oil byproducts that con high levels of such chemicals as th

Food Engineering, February 1976


MORE STATES REQUIRING IMPACT STUDIES

New York's Governor Carey has signed the Environmental Quality Review Bill requiring environmental impact statements all

Pollution Engineering, October 1975


Food Surveillance Bill passes Senate Commerce Committee

Only one change was added to the ood Surveillance Bill before it passed he Senate Commerce Committee. This ne change—regarding the

Canner/Packer, January 1976

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SPECIAL REPORT

Energy: the U.S. at the crossroads

In late 1973, when the effects of the petroleum embargo were beginning to make themselves felt, the federal administration called for U.S. energy independence by 1980. There was also considerable talk about a concerted energy policy. This led to the formation of a Federal Energy Office, later to become the Federal Energy Administration (FEA), and other ambitious deeds, plans, and hopes.

In fact, as *ES&T* 's Marty Malin pointed out (in a Special Report, May 1973, p 392), the U.S. had (and apparently still has) a *de facto* policy which "boils down to a basic goal—unlimited cheap energy." Escalating electricity prices, for example, have shown how effective this policy has been. To be sure, some legislators, including Sen. Jennings Randolph (D–W.Va.) and Sen. Henry Jackson (D–Wash.), warned that this goal was impossible. They also explained why rational programs of source diversification, conservation, and efficient energy use were of the essence, but not many took heed of these warnings. Now that one embargo has come and gone, and fuel prices have spiraled, a polite hearing seems, once again, to be given to pleas for conservation and diversification.

Meanwhile, one no longer thinks in terms of energy independence by 1980, or, for that matter, by 1985. Indeed, achieving a fairly embargo-invulnerable position by 1985 would be quite a feat. Dependence on petroleum imports has increased to more than 40% from perhaps 25–30% in pre-embargo mid-1973. Conservation policy is largely ill-defined, although, to be sure, many government and private institutions and companies, and public-spirited people, are voluntarily undertaking vigorous conservation measures. On balance, the U.S. effort to date to cut back its energy appetite can be said not to have made great progress.

Reduction of motor fuel use helps to clean the air.

Here's how well that worked in the Washington, D.C., area, so far, if one judges by air quality:

Year	Number of air pollution alerts[b]
1970[a]	1
1971[a]	1
1972	4
1973	6
Embargo	
1974	1
1975	4
1976[c]	5

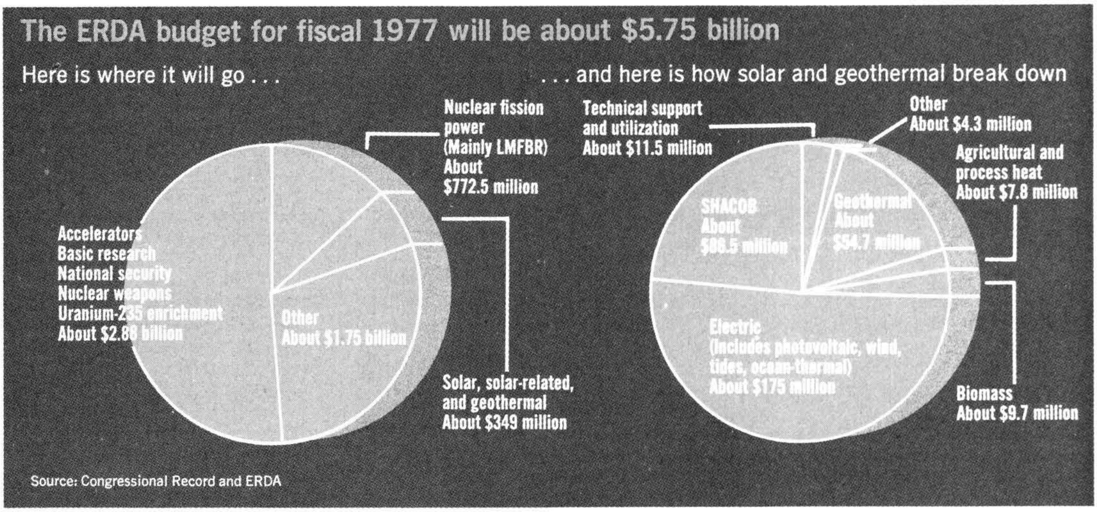
[a] Records were sketchy. [b] Compilation of air quality index figures began in 1973. [c] Through August 6. Note: Pollution around Washington is almost entirely of automotive origin. Source: Metropolitan Washington Council of Governments.

A "quick-fix" approach

The real essence of the present energy situation is economic; more specifically, it is found in the billions of dollars the U.S. must export annually to pay its oil bills. These dollars, if not exported, might, in part, have formed capital to create new products and jobs, to improve the environment, or to retire outstanding debts. In other words, the amount of cash and credit exported impoverishes the nation by that much.

Is there a "quick-fix" way of alleviating this situation? The answer is a guarded "yes," if one is not overly fussy about what time frame he may wish to assign to "quick-fix," and if one is prepared to accept certain sharp changes in life style and all that these changes imply.

This "quick-fix" approach is simply the type of industrial, residential, and



The ERDA budget for fiscal 1977 will be about $5.75 billion

Here is where it will go . . .

. . . and here is how solar and geothermal break down

Source: Congressional Record and ERDA

ES&T's Julian Josephson takes a look at what is going on under the sun about "renewable" sources of energy. They show promise, but have many problems, and much technology still needs to be proved

transportational energy conservation measures one normally associates with wartime austerity. Such measures could be justified by the notion that, because of the 1973–1974 embargo and subsequent cartel prices, the U.S. is engaged in a form of economic war with certain oil exporting countries. Unfortunately, aside from the various dislocations they may cause, draconian austerity measures can lead to bureaucratic bumbling, inequities in their imposition, and other well-known problems. A countervailing argument might be that mandatory austerity produces results more quickly and completely than does voluntary austerity. However, those who have lived through tight austerity periods often take issue with this latter argument, citing personal experience as their basis.

Actually, the measures just discussed involve what Charles Coutant of the Oak Ridge (Tenn.) National Laboratory (this issue, p 868) calls reductive energy conservation (car pooling, rationing or high taxes, and the like). True, with this type of conservation, less domestic and imported fuel is consumed per time unit. The U.S. balance of payments could be improved, and, as a bonus, air quality, for instance, may be enhanced. However, Coutant notes that reductive conservation may only momentarily slow energy use, without much affecting the long-term upward trend. He calls for rounding out the picture with *productive* energy conservation with which partially spent energy is put to further use.

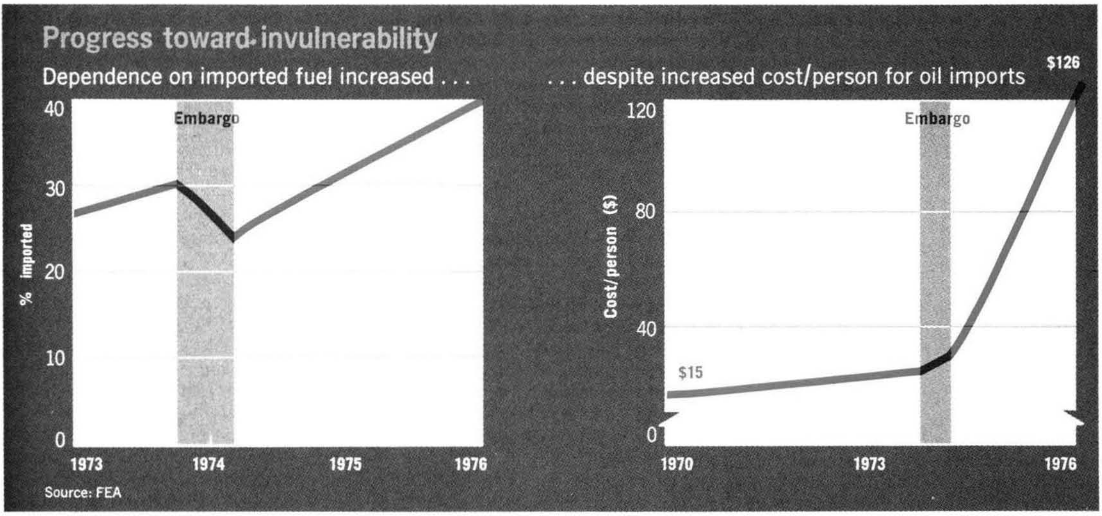
Nevertheless, conservation is the "quick-fix" (and non-polluting) approach, if one indeed exists, and probably the only one right now. There is a great deal heard about the environmentally acceptable, large-scale development of coal and nuclear power—much of which involves non-renewable energy sources. For an idea of how well that is going, one might consider that it is now estimated that even by 1985, for example, "clean" liquid fuels from coal will have no appreciable impact, according to the U.S. General Accounting Office. Original expectations were for a 2.5 million-bbl/d equivalent by then.

Time slippages, cost overruns, and other setbacks are also being experienced in the quest for oil from "far-out" sources, and in nuclear development. The Alaska pipeline and the Clinch River (Tenn.) liquid metal fast breeder reactor (LMFBR) are among the more notable cases in point. Still, it can be reasonably projected that the main thrust of energy source development will entail non-renewable petroleum, coal, and fissionable nuclear material, and that most of the renewable sources, with the possible exception of solar and perhaps geothermal, will be the subject of many more books and articles than of large-scale, practical engineering and commercialization.

Renewables

In a sense, there is no infinitely renewable source of energy. After all, the sun itself might cease to provide energy some billions of years from now. Nevertheless, there are very long-term sources. Plutonium breeding, for instance, is at least a multi-thousand-year source. Deuterium-deuterium fusion, if it ever proves feasible, can be seen as a billion-year source. Geothermal would be available as long as the earth's heat lasts; and solar energy and its derivatives, such as wind, ocean thermal gradients, waves and tides, biomass, and the like, should last as long as the sun itself.

If severe economic displacements are not to be experienced, additional non-renewable fossil and nuclear sources need to be developed with all due speed and safeguards. However, accelerated



Source: FEA

efforts should be made to bring the renewables to a state of high technology:

- to provide the most diversified mix possible, so that dependence upon one or two sources is no longer lopsided
- to obviate the unpleasant economic situation that would arise when non-renewables are exhausted.

And, unless the U.S. and world economy undergoes some very unforeseen changes, or some radical technological breakthrough occurs, exhaustion of the non-renewables is almost as sure as the proverbial death and taxes.

The know-how is here

In "Energy Earth and Everyone" (Books, *ES&T,* January 1976, p 86), the author, Medard Gabel, who led the World Game Workshop that helped to put that book together, characterizes non-renewables as "capital energy sources," and renewables as "income energy sources." In the foreword, R. Buckminster Fuller, one of the elder statesmen of environment and clean energy, asserts that the knowhow to harness the "income energy sources" by 1985 exists now. Fuller also says that use of these sources will afford mankind a higher standard of living and greater degree of freedom than ever previously experienced. All this can be attained even though further use or development of fossil, fission, and fusion energies is phased out by 1985, he noted.

Perhaps Fuller's view reflects a great deal of optimism. A contrasting view was expressed by W. Donham Crawford, president of the Edison Electric Institute (EEI, New York, N.Y.) at a Bermuda meeting of the Industrial Gas Cleaning Institute (IGCI) held earlier this year. Crawford said that the energy base of the U.S. is in a "transition period" from fossil to renewable resources (in which he included fusion). However, he told the IGCI meeting that such new energy sources will not play any significant role until after the turn of the century. In the meantime, coal and nuclear power must be used to sustain the U.S. through this period of change, he said.

In hot water

At least one "income source" seems to offer more than a ray of hope. When solar energy pioneer George Löf of Colorado State University received the $25 000 Lyndon Baines Johnson Foundation Award in February (*ES&T,* April 1976, p 315), he said that the use of solar energy for heating and cooling is "now a commercial reality." At least a reasonable facsimile of commercial reality exists, if one is to judge from the 45 exhibitors at the Second Annual Meeting of the Solar Energy Industries Association (SEIA, Washington, D.C.), held in Washington in mid-June. These exhibitors included large companies such as Ametek, GE, Grumman, Olin, PPG Industries, Revere Copper & Brass, and Westinghouse. Smaller firms with "track records," were also represented—InterTechnology Corp. (Warrenton, Va.) and Thomason Solar Homes (District Heights, Md.), to name a couple.

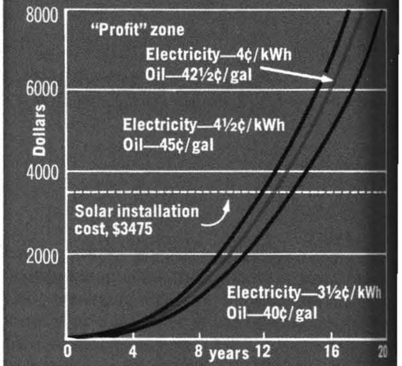
Products and systems on exhibit included collectors, heaters, photovoltaic cells, portable cookstoves, and publications. For example, Grumman (Bethpage, N.Y.) displayed its "Sunstream" domesticated hot water system. GE (Philadelphia, Pa.) had a solar-assisted heat pump. Ying Manufacturing Corp. (Gardena, Calif.) showed a patented solar heating/cooling system, and Ametek, Inc. (Hatfield, Pa.) offered a high-performance solar collector. Total Environmental Action (Harrisville, N.H.) was one of the book and solar component exhibitors, while Sam Nakhleh, president of Intercontinental Enterprises Corp. (Eastchester, N.Y.) was cooking French toast and "hot dogs" on a portable folding solar stove that accumulated energy from a floodlight, since the show was indoors.

Solar energy for heat and hot water, and even for cooling, is now available. For a U.S. first, Ametek provided 270 solar collectors (6500 ft^2) for heating and cooling of the $1 million Santa Clara (Calif.) community recreation center. The solar system itself cost about $500 000. About 40% of that cost is for monitoring equipment for the system and testing of the collectors. An additional $300 000, or so, will pay for a 1-yr monitoring program, as well as engineering and legal studies. The system will use a 140-gpm water flow for heating/cooling, a 10 000-gal hot-water reservoir, and a 50 000-gal cold-water reservoir.

Grumman's hot water system will be found in some homes on Long Island, (N.Y.). Solaron Corp. (Denver, Colo.), of which George Löf is vice president, had a $500 000 order backlog earlier this year, and was installing systems on 60 buildings in 12 states, as of the first quarter of this year. Thomason Solar Homes is licensing the "Solaris" system which, according to Harry Thomason, the company's president, provides material cost advantages in solar-heated/cooled home building and retrofitting, especially because of its design. For example, he explained how a solar heated/cooled home of his design would cost $42 000, while a competing home, with solar heating only, might cost $50 000.

Almost every day, one hears of a house, school, hamburger "joint," professional building, or other establishment "going solar." As Löf observed, solar is commercial. However, he predicted—and the present situation seems to bear his prediction out—that initial commercial use of solar energy will be found in heating, hot water, and cooling. Large-scale use of direct solar energy for electricity generation and mechanical applications will probably come about in the 21st century, barring some unexpected technological breakthrough.

Payback time for solar heating and hot water



Note: Single-family residence in Washington, D.C., area. Solar provides 40% of thermal energy requirements. Source: SEIA (Washington, D.C.)

The sun industry

Sheldon Butt, SEIA president, observed, as Löf had previously, that solar energy is here now and not down the road. While it is not red hot yet, it is warming up, and is not just in a research and development situation. Butt, who is also director of market research and planning for Olin Brass, Olin Corp. (East Alton, Ill.), provided a cash flow analysis for heat and hot water for a single-family residence in Washington, D.C. This residence would total 1500 ft^2, have 40% of its thermal energy requirements furnished by solar energy, and be amortized over 20 yrs. The installation cost is estimated at $3475; back-up hot water requirements are provided by electricity, and heating by oil. "Payback" from installation of this solar energy system could be 12–14 yrs, depending on the price of electricity and oil; after these time periods, the projection shows a "profit."

George Szego, president of InterTechnology Corp., and secretary of SEIA, reminded *ES&T* that three days of sunshine provide the world energy equal of all known fossil reserves. He projected oil equivalent savings of 1 million bbl/d, equivalent to $5 billion/yr, within 10–15 yrs, if a crash program in accelerated solar energy development were initiated now. Other benefits Szego foresaw were new jobs and export markets, and lessened needs for fuel imports and public utility capacity. He also said that "typical" solar installations could provide 60% of SHACOB (*s*olar *h*eating *a*nd *c*ooling *o*f *b*uildings) needs. Finally, Szego noted the existence of a double anti-pollution benefit that solar provides. First of all, solar does not pollute; secondly, pollution is obviated because other fuels, which would normally be used, are not used.

This anti-pollution benefit is especially important when one thinks of excess carbon dioxide (CO_2), with its "greenhouse effect," as a product when fossil fuels are burned. This is a controversial point; however, Szego observed that atmospheric CO_2 concentration averages 325 ppm worldwide. At present rates of fossil fuel combustion, this average could rise to 650 ppm in 25 yrs; in 35 yrs, the earth's average temperature would rise 1 °C, and in 75 yrs, 3 °C. This increase could bring about wholesale changes in climate, food production, and ocean level. He brought up this potential CO_2 threat as a principal reason why solar becomes necessary. The large coal deposits, he said, cannot all be used, whether raw, refined, gasified, or liquefied, under known technology, without raising world CO_2 levels beyond the danger point.

Thus, accelerated solar energy application is vital. For quicker SHACOB use of solar, SEIA is calling for tax incentives and loan guarantees. For example, a homeowner might have a tax credit of 40% of the first $2000, and 25% of the next $6000 invested in solar equipment that meets standards under development by the National Bureau of Standards, or to be developed by the American National Standards Institute. Other tax credit and rapid amortization plans were proposed for commercial/industrial organizations and non-profit institutions. A start in this direction has been made. California has granted a state income tax credit of 10% for solar equipment purchase/installation costs, to a maximum of $1000.

"Sunpower"

The SEIA meeting and other events and activities emphasize SHACOB for the immediate future. But what about the use of solar energy to generate electricity? Piet Bos, solar program manager for the Electric Power Research Institute (EPRI, Palo Alto, Calif.) does not foresee large-scale sunpower for this century. Even as far as total energy is concerned, U.S. Energy Research and Development Administration (ERDA) officials see solar as supplying only about 7% of U.S. energy needs by the year 2000, and maybe 15% by 2020.

Nevertheless, some effort for sunpower is here. One project involves the use of 320 large mirrors to reflect sunlight onto a boiler atop a 200-ft concrete tower. Sandia Laboratories (Albuquerque, N.Mex.) will pilot-test this "heliostat" boiler/generator for ERDA as a means of producing electricity. If results are favorable, ERDA hopes to complete a similar solar tower. An example of indirect or "secondary" use of solar for power, that tower would produce 10 MW—enough for a community of 10 000 people.

Solar cells convert sunlight directly to electricity ("primary" solar use). Unfortunately, ERDA estimates power generated by this means at $20/W. This cost must come down to 50¢/W if solar cells are to be competitive with other sources. ERDA's plans are to achieve that 50¢ figure by 1985. Joseph Lindmayer, president of Solarex Corp. (Rockville, Md.), a solar cell manufacturer, believes that by 1985, these cells will be commercially available for house and building rooftop electricity generation.

A principal stumbling block in solar cells, up to now, has been the expense of their manufacture. Basically, they must be

SHACOB at work

Where it is used	*Who is doing it*
Homes in Mass., N.H., and R.I.	**New England Electric System**
Homes on Long Island, N.Y.	**Grumman (Bethpage, N.Y.)**
Barefoot Mailman resort hotel, Broward County, Fla.	**High Plumbing (Pompano Beach, Fla.) and Solar Dynamics, Inc. (Hialeah, Fla.)**
Burger King, Voorhees, N.J.	**Northrup, Inc. and Arkla-Servel**
Burger King, Tallahassee, Fla.	**Aerocell Pollution Control, Inc. (Tallahassee)**
Dental clinic, Indianapolis, Ind.	**Solar Energy Products, Inc. (Avon Lake, Ohio)**
"Decade 80" solar house, Tucson, Ariz.	**Copper Development Association, Inc. (New York, N.Y.)**

Problems with "renewables"

In the temperate and tropical areas of the world, solar energy striking a horizontal surface can be 140–200+ kilolangleys/cm^2/yr. One langley is one calorie/cm^2. Thus, 200 kilolangleys work out to 0.21622 kWh/ft^2, or 603 million kWh/mi^2. In the U.S., midwestern regions might receive 140 kilolangleys, while the area of Tucson, Ariz., could receive 200+ kilolangleys, on the average. Harnessing this energy, however, poses some problems.

A main problem of solar, wind, and certain other "renewable" energy sources is that they are intermittent, diffuse, and of energy intensity or flux too low for the needs of most present technology. Another problem is efficient storage of heat or electrical energy against times when the sun, wind, or other "renewable" is temporarily unavailable.

Thus, one thrust of "renewables" R&D is to increase energy flux thermally, electrically, or mechanically. One example of this effort may be found at Odeillo, France, where a mirrored solar heater produces temperatures of up to 6000 °F and one MW/d of power. Another is the work in finding ways to mass-produce photovoltaic cells and materially raise their efficiency; reputedly, Mobil-Tyco has made a breakthrough in the mass production direction. For wind, the push may be toward increasing mechanical efficiency of the devices, and improved electrical inversion. Batteries, heat pumps, hot water vessels, and other approaches are among subjects of storage R&D.

With respect to high energy flux, incidentally, coal presents an irony. Here, solar energy was rather inefficiently converted and stored as organic chemicals in biomass, which itself was later changed to coal, which, because of the subterranean heat and pressure to which it was subjected for long ages, now furnishes a high energy flux. In effect, the energy receipt, conversion, and storage were of very low efficiency and intensity. The real concentrating factor was geologic time.

Indeed, if one wants to arrange for the right types of plant biomass and environments for them, and subsequent subterranean pressure cooking, one may then consider coal to be a renewable energy source. All that is then needed is a high degree of patience on one's part until the coal is ready for use.

made of highly refined silicon, which is then "doped" with impurities such as boron, which is necessary to impart photovoltaic characteristics to the cell. Each cell must then be hand-cut and shaped to prescribed sizes and forms, and arranged in a predetermined pattern. However, Mobil-Tyco Solar Energy Corp. is working on a method to mass-produce and cut the time necessary to make cells—from silicon purification and "doping" to the formation and arrangement of the cells. Apparently promising alternatives to silicon cells, such as gallium arsenide (Ga-As) and cadmium sulfide (CdS) cells are subjects of federally funded R&D.

Some "renewables" projects

Energy source	Activity or approach	Agency/ company
Ocean-thermal	Floating power plant study	ERDA/Lockheed Missiles and Space Co. (Sunnyvale, Calif.)
Ocean-thermal	Floating power plant study	ERDA/TRW, Inc. (Redondo Beach, Calif.)
Tides	Study, 9 mos, Passamaquoddy Bay, Me., and Cook Inlet, Alaska	ERDA/Stone & Webster (Boston, Mass.)
Wind	Wind turbine generator, 100 MW, Sandusky, Ohio	NASA/LeRC (Cleveland, Ohio)
	Wind-powered generator, vertical axis	ERDA/Sandia Laboratories (Albuquerque, N.Mex.)

Sandia tried the approach of using a lens to focus sunlight on a silicon cell 2 in. in diameter. This procedure apparently raised the cell output from $\frac{1}{5}$ W to 10 W. A system of 150 lenses and 150 cells could produce 1 kW of electric power, and that goal is what Sandia was aiming for this summer.

Another possibility is the concentration of solar heat from concave aluminum reflectors on a system containing a fluid such as toluene. The toluene is vaporized and drives a turbine to generate electricity; spent vapor recondenses, and the cycle is repeated. Sandia is also trying this method with about twenty 9 by 12 ft reflectors to provide the necessary heat.

Another stumbling block for sunpower is energy storage, so that power can be provided by night, or during periods when the sun does not shine. This storage could be in the form of batteries or heat, and the technology still needs developing. For example, for the Sandia 10-MW heliostat system, Honeywell Inc., Martin Marietta Corp., and McDonnell Douglas Corp., are working on heat storage systems good for 4–6 h. At present, according to ERDA consensus spokesmen, attempts to increase this storage time would raise the costs "out of sight."

Finally, cell conversion efficiency needs to be perfected. Generally, photovoltaic efficiency runs 10–12%. This year, higher efficiencies—perhaps up to 20%—have been reported. A main objective of solar R&D is to improve cell efficiency. The Sandia conversion/heat technique may be one answer; cells of different chemical compositions may be another.

Blow ye winds, heigh-ho!

Wind may be regarded as a form of solar energy, since the sun's action on the atmosphere is the ultimate cause of winds. Its use as a power source is not exactly new; for example, at Grandpa's Knob, Vt., in 1941, a wind turbine, 175 ft in diameter, produced 1.25 MW at a cost (1945 dollars) of 3 mils/kW vs. 2.5–6 mils/kW for fossil-fueled power plants. The energy from wind at Oklahoma City, for example, averages 18.5 W/ft^2 of area perpendicular to the wind, approximately equivalent to the solar energy/ft^2 of land in that area.

Near Sandusky, Ohio, NASA's Lewis Research Center (Cleveland) is experimenting with a wind turbine generator (WTG) that can produce up to 100 kW with an 18-mph wind. Blade diameter is 125 ft; there are two 62.5-ft blades, each of which weigh 2000 lbs. Cost is estimated at $5500/kW; follow-on 200-kW systems may run $2340/kW. Also, vertical-axis systems are under development by NASA, Sandia, and others.

Do you want to be the first in your neighborhood with a wind energy conversion system (WECS)? Enertech (Norwich, Vt.), one of several firms, carriers WECS and auxiliary equipment for the home, farm, and business needing an alternate energy source. One system, priced at $16 200 with inverter, will produce 200–310 kWh in an 8-mph wind, and 600–930 kWh in 16-mph wind. It provides 115 VAC, and comes with a 40-ft galvanized steel tower and 115-VDC, 450-amp-h batteries.

Some electric utilities are interested in wind energy. Indeed, ERDA has asked 17 of them to monitor wind in their respective areas. The results of this monitoring should lead to four or five being selected for further work in development of wind energy as a power source.

Ups and downs

In a number of places tides range 20 ft and more. These include the Bay of Fundy (Me., and Canada), western France and England, the Yellow Sea coast of Korea, and the U.S.S.R.'s White Sea.

The best-known use of tidal power is at La Rance, France, where tides help to generate 240 MW of power. At Mezen, on the U.S.S.R.'s White Sea, a 1.5-MW plant, the initial phase of a network that would generate 6 MW, is being built. There is also much talk about an 800-MW tidal plant for the Severn River, England, and about large-scale use of tidal power at Passamaquoddy Bay, Me. So far, these plants are still mainly in the talk stage. However, in April, ERDA did allocate $168 733 for a 9-mo study of tidal power at Passamaquoddy Bay, and Cook Inlet, Alaska. Stone and Webster (Boston, Mass.) is doing that study.

Great Britain may be placing a bet on wave energy with a Department of Industry grant equivalent to about $114 000 to test out "Salter's ducks." These are a string of vanes, devised by Stephen Salter of Edinburgh University, which are shaped to extract a high percentage of sea wave energy. Engineer Eric Wood has designed a means by which not only would the vane string array not be broken by the waves, but energy extraction would be level.

The British Department of Energy is also supporting wave-energy projects. That department estimates that 10 years must pass before a 10-MW prototype ocean-wave electric generator is operational, and that a 1000-MW station could not come on line before 1996. However, Salter, who is also with Sea Energy Associates, a part of Ready Mixed Concrete Ltd. (also supporting the "duck" project), believes that his system could actually be making money in five years.

On a small scale, the use of temperature differences between the warm ocean surface in tropical waters, and the colder depths have been used as power sources. Cuba (40 kW, 1930) and the Ivory Coast, Africa (7 MW, 1950s) were the sites. Essentially, this approach used a fluid such as ammonia or propane that vaporizes in

For a closer look at "renewables" . . .

"Solar Industry," by Carolyn Pesko
Ann Arbor Science Publishers, Inc.
P.O. Box 1425
Ann Arbor, MI 48106

This book lists "who does or makes what" in the solar industry.

"Solar Energy for Heating and Cooling of Buildings," by Arthur R. Patton

"Thermal Energy from the Sea," by Arthur W. Hagen
Noyes Data Corp.
Mill Road at Grand Avenue
Park Ridge, NJ 07656

These are state-of-the-art reviews in their respective fields.

"Wind Machines," by Frank R. Eldridge
Stock Number 038-000-00272-4
Superintendent of Documents
U.S. Government Printing Office
Washington, DC 20402

Wind devices, past and present, are described, and prospects are discussed.

the warmer depths to drive a turbine, and then condenses in the colder depths, 2000–3000 ft, for example.

For fiscal 1974, the National Science Foundation (NSF) awarded $500 000 for ocean-thermal work; NSF funding was $2 million in fiscal 1975. For fiscal 1977, ocean-thermal is included in ERDA's $175 million solar/electric funding. The Johns Hopkins University Applied Physics Laboratory pegged total costs of developing a 100-MW demonstration ocean-thermal plant at $96 million (*ES&T*, February 1975, p 104).

A head of steam

Geothermal power first came into service at Larderello, Italy, in 1904. Now, the Larderello plant is almost 406 MW, and contributes materially to powering the FSI (Italian railroad). In California, at "The Geysers," Pacific Gas and Electric Co. (PG&E) uses dry geothermal steam to provide 502 MW (ultimate capacity could approach 2000 MW) for 5% of the needs of PG&E's 3 million customers in northern and central California. Other geothermal sites are in use or under construction in France, Iceland, Japan, Mexico, New Zealand, and the U.S.S.R., or are being planned or contemplated in those countries, as well as El Salvador (UN project), and in California, Idaho, Oregon, and Texas.

Ideally, a geothermal source would be dry, clean steam. Hot water, however, could also be a source. The latter will be looked to increasingly, since it is more abundant. Unfortunately, much of this water is mineral-rich, and corrosive, abrasive, and hard on equipment. There is also potential for release of ammonia and sulfurous gases. Nevertheless, "teakettle power" (*ES&T*, August 1973, p 680) is plentiful, and if 13% of its total heat were converted to electricity, about 10 times the world's present power output (580 trillion kWh) could theoretically be produced.

On a lighter note . . .

Amid the energy hubbub, there are papers and conversations concerning possible conversion from fossil to hydrogen (H_2) fuel (*ES&T*, February 1975, p 102). And why not? In principle, H_2 burns cleanly, with water as its combustion product. H_2 abounds on earth. True, H_2 is hazardous, but so is natural gas if improperly stored, transmitted, and used. Hydrogen might be stored as a gas under pressure, as a cryogenic liquid, or as hydrides.

H_2 systems were the central topic of the 1st World Hydrogen Energy Conference, held in early March at Miami Beach, Fla. This conference was sponsored by ERDA and the University of Miami (UM), and chaired by UM professor T. Nejat Veziroğlu. Among topics discussed were nuclear, solar, fossil-fuel, and other approaches to H_2 production; conversion to an H_2 economy; and H_2 applications, some of which are quite advanced in concept. For example, Roger Billings of Billings Energy Research Corp. (Provo, Utah) proposes an H_2-fueled mass transit system using 21-passenger buses. Fuel storage would involve metal-hydride containers made of an iron-titanium alloy.

Other H_2 applications described involved conversion of a U.S. Postal Service mail truck to this fuel at the University of California (Los Angeles), and its good safety record despite an overturn at 20 mph. The fuel source was liquid H_2. The 3-volume Conference Proceedings (*ES&T*, May 1976, p 498) provides an insight into how far theoretical and practical work in H_2 energy has progressed.

Audacious prophecies

The foregoing discussion, at a very fast gallop, indicates some options that the U.S. has in its transition from non-renewables to renewables. It did not include fusion, solid waste, methanol, or other sources which, it was felt, are appropriate for other articles. Also not included are sources whose technology is in such a state of infancy as not to constitute a plausible option at this time. This category would include use of ocean currents, deep ocean pressure, and phase transformation.

Concerning the "transition period" of EEI's Crawford, *ES&T* makes the audacious prophecy that this period will be a very long one—well into the next century. Perhaps, clean, renewable sources will be part of an energy mix as this century draws to a close, but they will have the smaller share of this mix. The main thrust of energy development will remain fossil and nuclear.

For the nearer term, 5–10 yrs, *ES&T* brazenly prophesizes that U.S. vulnerability to the effects of a petroleum embargo will not lessen appreciably. Despite all the "pep talks" and "hoopla," this vulnerability could still exist in 1985 though, perhaps, less in degree by then.

Concerning a new embargo, hopefully, somewhere in Washington, there exist countermeasure plans. These plans should be based on the assumption that it will be long, widespread, complete, and efficiently policed by its perpetrators; and that the much-touted international plans to combat it will come unglued in an every-nation-for-itself scenario. As for renewable energy sources, there needs to be much more accelerated development, not only as a hedge against embargoes, but also to provide a rational, highly competitive and diversified energy source mix, and to husband carefully the finite and decreasingly accessible resources that exist on Spaceship Earth.

Some more audacious prophecies

- ***Many more energy conservation programs will be in the industrial and commercial areas, rather than in the transportation sector. Indeed, conservation in the transportation sector will continue to lag far behind that of the other areas.***
- ***There will be another oil embargo. Moreover, it will be more widespread and "leak-resistant" than the 1973–1974 embargo was, and it will last for a considerable time after its underlying political cause has ended. Its end will not be an abrupt lifting, but rather, an irregularly-staged phaseout. Hopefully, this prediction is dead wrong, and equally hopefully, there will be national plans made as though this prediction were right "on target."***

How trash is being turned into useful heat

The John Deere Co. uses pyrolysis and heat recovery to meet 75% of its needs for paint drying ovens

The John Deere Horicon Works is a division of Deere and Company, one of the largest 100 corporations in the U.S., with annual sales of more than \$2.96 billion. The Horicon Works produces Deere's line of lawn and garden equipment and snowmobiles.

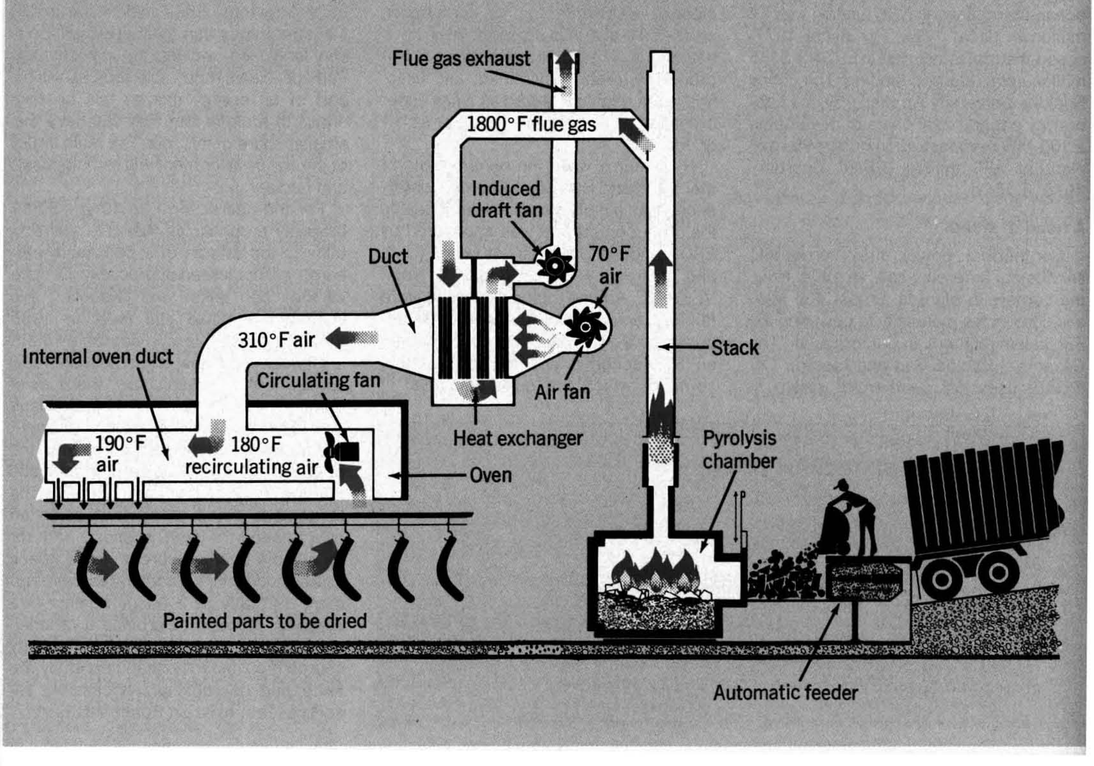
Its Horicon Works generates some 3300 tons of trash each year. The mix is 50% lumber, 10% plastic, and 40% miscellaneous. In the past, the corrugated waste was baled and sold. On a contract basis, today it would cost the company \$38 400 a year to dispose of its waste, but when the Horicon landfill was closed by the local authorities in 1974, the company ventured into a field of new technology.

To combat the natural gas shortage and rising fuel bills, the company started burning its own trash and garbage—generating enough heat energy to save more than 14.6 million ft^3 of natural gas annually.

Dwayne D. Trautman, manager of process and tool engineering for the Deere plant says, "In the process, the company will save \$52 000 a year in both fuel bills and hauling costs. Considering that the entire installation for recovering this otherwise wasted energy will cost \$110 000, the company will realize a substantial return (45%) on its initial investment—a rather unusual payoff for a new technology."

Trautman continues, "By combining pyrolysis with heat recovery, we are bringing about the 'marriage' of two known technologies and thus have dis-

Pyrolysis with heat recovery, how it works



covered a new source of energy right on our doorstep—one that we had previously been paying people to take away and burn in the ground. At today's price for oil, and projected prices for gas, the garbage and trash we used to haul away is now worth between \$7–10/ton in recoverable energy."

How it works

The heat is created in a pyrolysis waste disposal system designed by Kelley Co. (Milwaukee, Wis.) in which a combustible gas is generated in the primary burning chamber. As a result, the process literally "burns up its own smoke", and emissions are far below air pollution control standards set by environmental protection agencies.

Through its representative, Paul Reilly Co., the Kelley Co. also supplied the heat recovery unit that generates 3.9 million Btu/h, providing heat for 30 000 ft^2 of paint drying oven area. This heat cut Deere's consumption of natural gas by more than 14.6 ft^3/year, or 75% of its total yearly gas consumption in the oven.

Kelley Co. vice president Robert Pfleger estimated that 720 trillion Btu recovered annually from the nation's 198 million tons of combustible solid waste would heat 2.4 million homes for a year in a northern climate. He says, "Every Btu saved by industry through the use of onsite heat recovery from the pyrolysis of solid waste saves energy for use in our homes. It also helps industry hold the line on costs and thus keeps inflation under control."

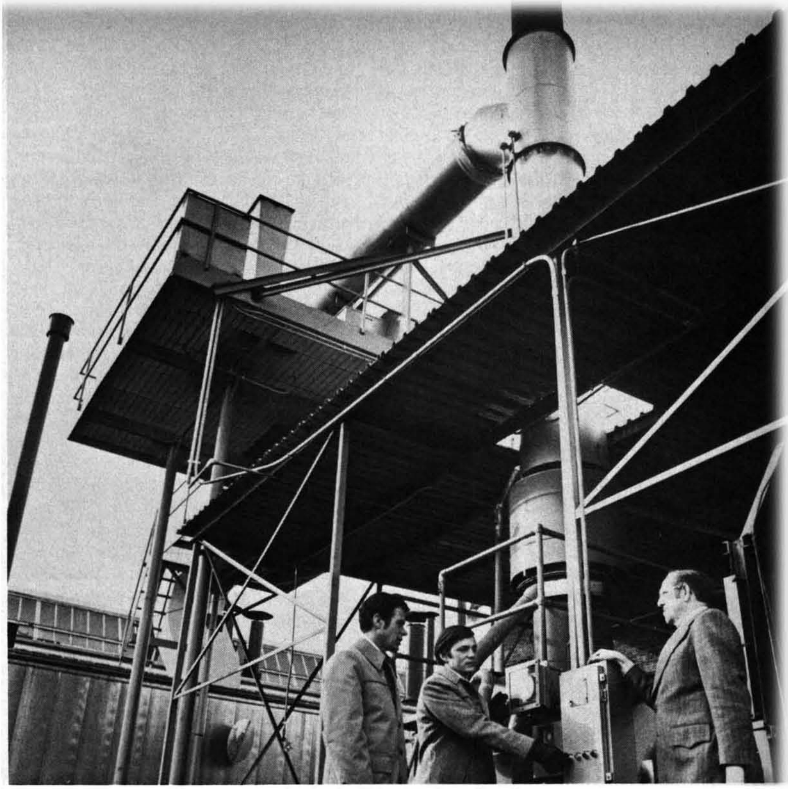
Savings

The pyrolytic system has been burning 2000 lbs of trash each day since September 1974. The unit, at that time, eliminated an expenditure of \$33 000 a year for hauling wastes to the nearest landfill.

According to the estimate of Wisconsin Power and Light Co. (Madison), suppliers of gas to the Horicon Works, this recovered energy would be enough to heat more than 90 homes in Wisconsin's climate for a year.

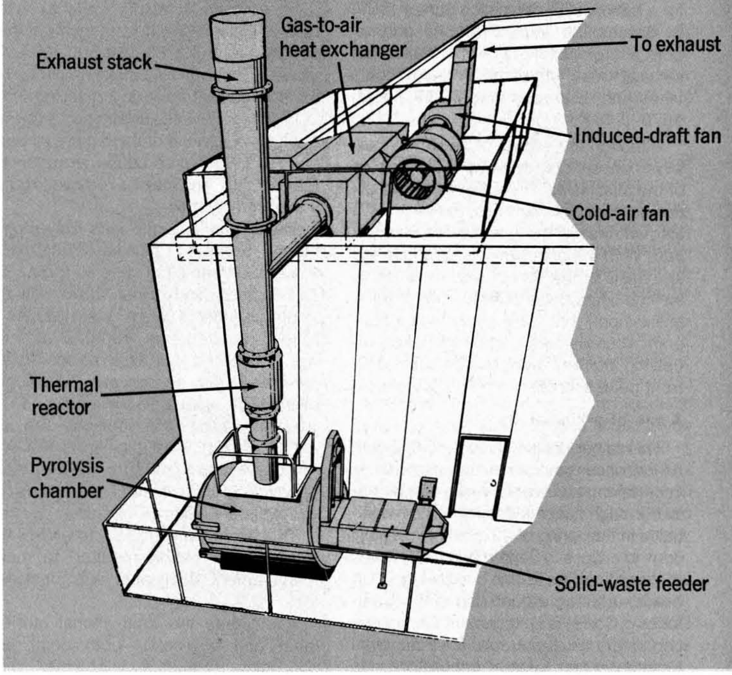
Supervisor of Engineering Services Karl Eberle projected that the dollar savings in fuel cost alone for the first full year of operation (1976) would be more than \$19 000. For 1977 and 1978, the savings will be \$2000 and \$27 000, for a 3-yr total savings in fuel costs alone of \$70 000. This is approximately the entire cost of the heat recovery unit. Even greater annual savings will be realized as gas prices continue to increase.

The only gas used now by the Horicon Works is for a pilot light in the incinerator's afterburner, and the remaining 25% of the energy needed directly to heat their drying oven, according to George Gibert, director of mechanical engineering, Wisconsin Power & Light Co.



Heat source. *Its fuel will be trash and garbage*

Typical flue gas-air heat recovery systems for industrial plants



OUTLOOK

Surveying America's lakes

EPA finds most U.S. lakes eutrophic, but one project shows how some may be restored to higher quality

Treatment plant. *Tertiary treatment removes the phosphorus from Ely's wastewater collected in these large chambers*

After all the chemical horror tales that have been brought to the public's attention in recent months, it might be difficult to recall that relatively innocent environmental age in the early 1970's when one of the major news flaps was the accelerated aging of America's lakes. The culprit was suspected as being phosphates in the municipal waste discharge including those in detergents.

With such extensive press coverage in 1972, William Ruckleshaus, then administrator of the EPA, countered by calling for a National Eutrophication Survey (NES) to assess the impact of phosphorus-containing effluents from municipal sewage treatment plants on the nation's lakes and reservoirs (see *ES&T,* March 1973, p 198).

Although the efforts of the first years were concentrated on sampling lakes east of the Mississippi River that received effluents from point sources, the year 1972 also witnessed the passage of P.L. 92-500. With the enactment of this law, the emphasis of the survey was modified to include lakes and tributaries (west of the Mississippi) that were impacted by non-point sources alone, although lakes receiving nutrient contributions primarily from point sources were still sampled.

A one-of-a-kind study

This rather unique survey—only South Africa, under government sponsorship, is undertaking an inventory of a similar nature though not of the same scope—initiated in the spring of 1972 will essentially draw to a close in September 1977. It was a coordinative effort involving EPA headquarter's staff and two field laboratories—Corvallis Environmental Research Laboratory and Las Vegas Environmental Monitoring and Support Laboratory—as well as every National Guard in the 48 contiguous states. EPA received the cooperation of state pollution control agencies and other state agencies concerned with managing fisheries, water resources or public health.

All the field work was completed in December 1975. EPA is now evaluating the data for eventual inclusion in summary reports that will be produced for each lake surveyed. To date, 359 final reports have been prepared, and another 213 are in draft stage.

These reports, made available to the states, will certainly help them meet their obligations under P.L. 92-500. EPA regional offices will also make ample use of the collected information in fulfilling some of their requirements under this same law. Furthermore, most of the data have been entered in EPA's computer storage system STORET and may be retrieved by any interested scientist.

The survey's scope was truly monumental. Some 812 plus lakes and reservoirs, 4200 sampling sites on tributaries and outlets, and about 1000 sewage treatment plants were sampled. As a rough approximation, 100 000 samples were collected and assayed for eleven parameters plus an algal assay developed by the EPA, several universities, and The Soap and Detergent Association. The cost for all of this? Best estimates are $12 million—about $15 000/body of water—of which $4 million was assumed by the various state National Guards.

The survey, undertaken to gather the type of information required to make management decisions, was designed to:

- estimate the total annual nutrient input and source(s)—both point and non-point—to each body of water
- evaluate the trophic condition (level of productivity and water quality) of the lake or reservoir at the time of sampling
- determine the nutrient—phosphorus, nitrogen, or some other element—that is limiting for the productivity of the body of water.

Determination of the limiting nutrient by using the algal assay or the nitrogen/phosphorus ratio is an indication of the potential for controllability. Obviously, if the limiting nutrient is, or can be made to be, phosphorus, and the source of this element is the effluent of a sewage treatment plant, then removal of the phosphorus from the effluent or divergence of the effluent from the final receiving water may restore higher water quality or at least retard eutrophication.

General findings

Since each lake surveyed has some unique characteristics, generalizations are difficult to develop without considering the basic lake type. However, useful relationships become apparent when lakes with similar properties are compared. Perhaps when all the data are compiled, the percentage of lakes that may be improved by point or nonpoint source control will be identifiable. At first glance, however, the findings are not worse than anticipated, claim Jack Gakstatter, chief, Special Studies Branch, and Marvin Allum, aquatic biologist, both involved with Corvallis' input to the NES.

An indication of the rather discouraging state of the nation's lakes appeared in a preliminary study published in 1971 under the title "Problem Lakes in the United States" (EPA Water Pollution Control Research Series). Unfortunately, the NES tends to confirm these earlier findings: In the first two years of the survey, 80% of the lakes and reservoirs in the eastern U.S. were found to be eutrophic!

A valuable data base

Dismal as the findings may be, Gakstatter, Allum, and Victor Lambou, chief, Water and Land Quality Branch, Las Vegas, feel that the survey provides the most unique water quality data base in the world. They point out that the data were compiled from analyses of water samples collected from nearly every state in the union, and that all samples were collected in the same way and analyzed by the same methods.

For many lakes, the survey will supply the only information available on them. Most importantly, the survey will establish a baseline against which the states can monitor the future improvement or deterioration of their lakes.

State agencies and EPA regional offices are putting the data to more immediate use, however. Twelve sections of the Federal Water Pollution Control Act Amendments of 1972 have been identified for which survey data can be used to meet compliance. As one example, section 314 of P.L. 92-500 requires each state to classify all publicly-owned water bodies, and provides for matching funds should states seek financial assistance.

If nothing else, the survey will assist the states in classifying their lakes; the data will also enable the states to decide what kind of treatment is needed to enhance the condition of a particular lake or waste treatment plant. The survey will also supply the states the data needed to support their requests for matching funds. It is not surprising, therefore, that many states are clamoring for advanced lake reports!

While the EPA scientists state that the collected data may not be the most refined—that, for instance, the data cannot be used to explain week-to-week fluctuations in water parameters—they are absolutely confident that the data are good enough to ascertain trends, to approximate the current status of the water body and to identify the source(s) of the problem should the lake or reservoir be eutrophic. And these, after all, were the goals the survey set out to accomplish.

Winding down

For the Corvallis laboratory, survey activities are drawing to a close. Corvallis is evaluating and validating the data and is in the process of performing general analyses of the effects of land-use practices on bodies of fresh water. The ultimate aim of all these manipulations is, of course, descriptions of the relationships between nutrient levels and lake responses. The data have already passed to modelers who are busy developing and testing lake and stream loading models.

Although Gakstatter and Allum admit that EPA could conceivably manipulate the collected data for years to come, they emphatically insist that Corvallis' involvement in the NES will come to an end by September 1977. In fact, the Corvallis group has begun studying the impact of nonpoint sources on the water quality of streams.

According to Lambou, however, Las Vegas' work will continue beyond the fall of 1977. Las Vegas will publish additional reports on factors affecting productivity and on lake problems such as aquatic weeds and fish kills. Using comprehensive phytoplankton data, Lambou and his group will calculate pollution indices for lakes in each state surveyed. Some of these latter reports become available this month. It is Lambou's contention that an "intensive look at the data is warranted for at least another two-year period."

A step beyond the survey

Once a lake is found to be eutrophic and the limiting nutrient identified, some action may be available that when taken may retard the aging process and even restore the lake as a recreational resource. One lake that has been successfully used for such a demonstration is Shagawa Lake near Ely, Minn.

The Shagawa Lake project actually predated the NES. The project was initiated in 1966 under the Federal Water Pollution Control Administration's (FWPCA) National Eutrophication Research Program to demonstrate the restoration of a eutrophic lake by removal of a limiting algal growth-promoting nutrient—in this case, phosphorus. An advanced (tertiary) treatment facility was constructed to remove the phosphorus from the municipal sewage while still allowing the treated effluent to flow into the lake.

Shagawa Lake, adjacent to the city of Ely (pop. 5000) in northeastern Minnesota, was an anomaly: Here was a eutrophic lake with a long history of algal blooms in a land of a thousand pristine lakes. Since the area had no significant agricultural or industrial enterprises, it was assumed that Ely's municipal wastewater, which had been discharged to the lake since before the turn of the century, was the major source of nutrients.

Once tapped as the source of potable water, Ely had to discontinue drawing water from Shagawa as early as 1932 when it turned to nearby Burntside Lake for its drinking water. Even after the in-

Shagawa Lake. Once prevalent algal blooms (insert) no longer are seen and the lake is once again recreational resource

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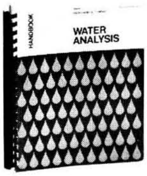

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CIRCLE 7 ON READER SERVICE CARD

stallation of a secondary treatment system (high-rate trickling filter) in 1954, the lake continued to deteriorate and soon lost its value as a recreational resource.

Demonstrating feasibility

So in 1966 EPA's predecessor agency, the FWPCA, built a pilot plant to remove phosphorus from a portion of Ely's wastewater to demonstrate that the treated effluent would have low algal growth-promoting potential. Based on the results of these studies, the EPA in 1971 funded a full-scale advanced wastewater treatment system that came on-line in 1973.

Through chemical treatment, this tertiary treatment system removes more than 99% of the phosphorus. The effluent flowing into Shagawa contains only 0.05 mg/l of phosphorus, a concentration not likely to significantly stimulate algal growth after its dilution with natural lake water.

Since 1966, chemical, physical and biological parameters have been studied to assess the recovery of the lake after nutrient reduction by advanced wastewater treatment. Shagawa is in the process of repairing itself but has not reached equilibrium, according to the Corvallis scientists studying the ecological responses. The lake's phosphorus concentration is not declining as rapidly as previously anticipated, and the scientists believe that they are witnessing feedback mechanisms. Here internal sources of phosphorus, perhaps from lake sediments or aquatic plants growing along the shoreline, may be leaching phosphorus to the water to retard the restoration process.

This project has demonstrated that a full-scale plant to remove phosphorus can be operated successfully. It has shown that phosphorus levels as low as 0.05 mg/l can be achieved through lime precipitation, and that the effluent containing these low levels may continue to flow into the receiving lake and still permit restoration processes to occur.

Financial woes

The EPA (Cincinnati) has operated the full-scale treatment plant for three years now. (Corvallis has studied the ecological responses of the lake.) Construction and operation costs through September 1976 total about $2.7 million, of which EPA provided 95% and Ely, 5%. EPA is scheduled to reduce its funding of the project this year. Ely says that it does not have the financial wherewithal to continue operation of the plant, and without outside financial assistance will have to shut it down.

Should sufficient federal funds not be found for the continued operation of the plant, A. F. Bartsch, director of the Corvallis laboratory, says that his scientists will continue to study Shagawa Lake, if only to observe the return of the eutrophic condition. LRE

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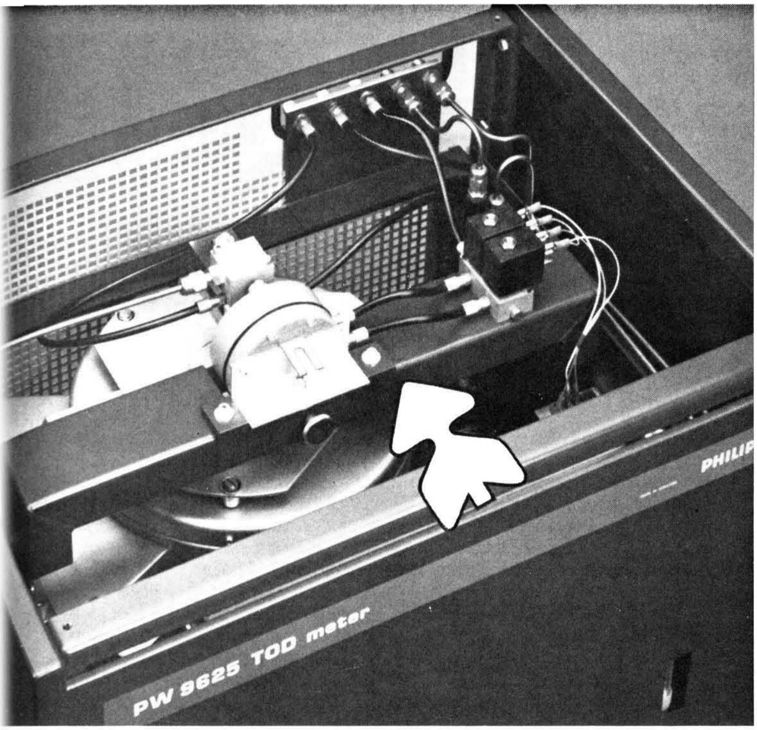

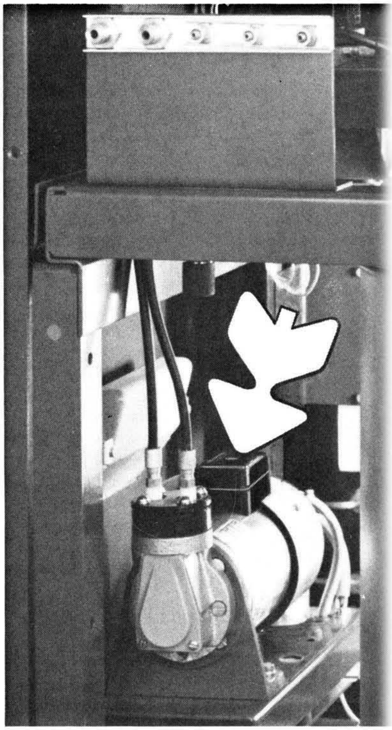

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The air cleaning equipment people

Since 1960, the IGCI has sustained an impressive track record in total sales and technology advancement

The technical trade association IGCI—the Industrial Gas Cleaning Institute (Stamford, Conn.)—represents member companies that design, manufacture, and install air pollution control equipment for stationary sources. This equipment represents the five areas of air cleaning—electrostatic precipitators, fabric filters, wet scrubbers, mechanical collectors, and gaseous emission controls.

Robert J. Wright, the IGCI president, succeeded E. P. Stastny on May 11 at IGCI's annual meeting. Wright is also general manager of the Fuller Company-Dracco Products (Catasauqua, Pa.), one of the member companies. Wright noted that order bookings for the member companies for calendar year 1975 were less than the previous year (*ES&T*, June 1975, p 516).

Three companies joined; the new ones are TRW Energy and Environmental Systems (Redondo Beach, Calif.), manufacturer of the "CDS" charged droplet scrubber; Young Industries (Muncie, Pa.), a manufacturer of fabric filters and mechanical collectors; and the Surface Combustion Division of Midland Ross Corp. (Toledo, Ohio), a manufacturer of thermal incinerators for hydrocarbon emissions and other gaseous controls.

Wright reports that the trade association bare hardware bookings (net F.O.B. shop) in 1975 were almost $375 million, a drop from the previous year but higher than 1973 bookings. These figures represent new orders for flange-to-flange equipment for installation in the U.S. and Canada. They do not include auxiliary equipment, ductwork, or erection.

Concerned primarily with industrial emissions from stationary sources, more than half of the dollar value of IGCI orders booked are in the area of electric utility power plants; the other half involve all other industrial emissions, including steel, cement, and paper.

Wright explains that there are several reasons why the 1975 bookings were less then the previous year:

- recession—during the recent recession, the steel, non-ferrous metals and cement industries have all been through a period of restricted capital expenditures, resulting in a reduction of new orders for air pollution control installations.
- a wait-and-see attitude by industry—waiting for the final words on the clean air act amendments before both houses of Congress
- the air cleaning equipment people passed the peak in the retrofit business (upgrading of older, existing installations) in the electric power industry.

Activities

One important project is represented by the fabric filter division explosion venting task group. The group started two years ago studying the problem of venting explosions to prevent equipment damage and personnel injury. "Wherever organic dusts are collected by fabric filters, there is a risk of explosion," Wright says. "We know more about the problem today than we did two years ago."

The task group upgraded the level of understanding in the industry and can now approach explosion hazards in a logical and predictive way. IGCI plans to sponsor a seminar on the subject of explosion venting and is seeking co-sponsorship among other interested associations and professional groups.

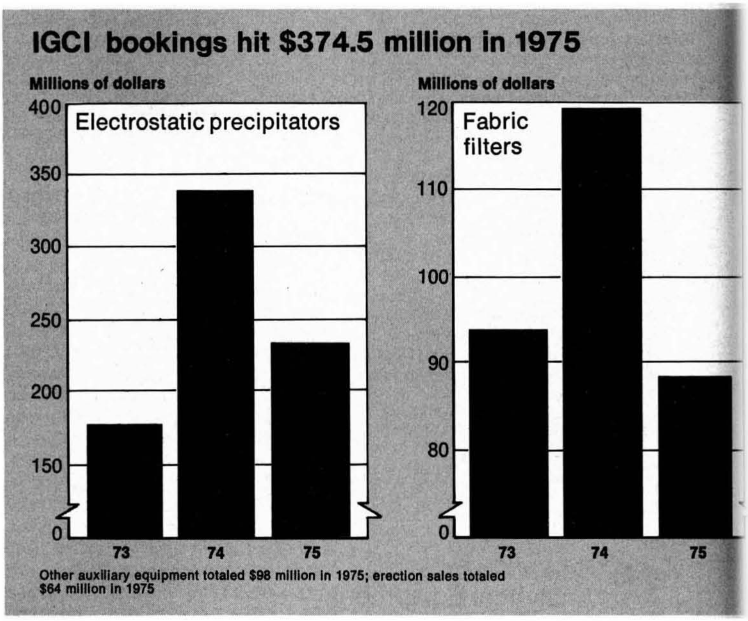
In the area of NO_x control, most of the work in the U.S. has been done by the major boiler manufacturers, in cooperation with the electric utility companies. This work involves modified combustion and reduction of flame temperature by one of several means. Lowering the flame temperature 800 °F, for example, from 3600 °F to 2800 °F, cuts the NO_x generation in half.

For the past six years, IGCI has been under contract with the EPA and its predecessor agency to identify preferred control technology and the associated costs for a variety of specific industrial emission sources.

Contract assignments of interest to *ES&T* readers include:

- mixed fuel firing—15% of Btu content from classified municipal refuse and 85% from pulverized coal in utility boilers
- emission controls cost for vinyl chloride manufacturing
- emission controls for the taconite processing and pelletizing industry. After comprehensive studies by Reserve Mining (Silver Bay, Minn.) and others, costs were examined for wet scrubbers, electrostatic precipitators, and fabric filters. In a proposed change to land disposal of tailings at the Reserve installation, fabric filters were selected by the company and approved by the state and federal control agencies.

As EPA cost studies are completed by IGCI in draft form, EPA has recently obtained user industry input by a three-way



Other auxiliary equipment totaled $98 million in 1975; erection sales totaled $64 million in 1975 meeting involving EPA, the IGCI working group, and teams such as vinyl chloride manufacturers, Ferro Alloy Association, AISI Sinter Committee, and the Fertilizer Institute.

Information exchange

Individual members of the companies represented in IGCI have been involved in the U.S.-U.S.S.R. Technology Exchange (*ES&T*, May 1976, p 414). Recent interest has focused on fine particle control technology and inspection of plants in the cement industry. This March, four Soviet engineers inspected three control systems in six cement plants in the U.S. Individual IGCI representatives returned the visit in June. The IGCI was represented by Frank R. Culhane, Vice President (also V.P., Int. Operations, Wheelabrator-Frye, Inc.); William V. Rice, V.P.; General Manager, MikroPul/U.S. Filter; and John Thomas, International Systems Manager, American Air Filter.

In the course of a year, the IGCI becomes involved with many different activities. The IGCI met with Canadian air pollution control equipment makers (AAPCEM, Association of Air Pollution Control Equipment Manufacturers) in Toronto. IGCI also met with its British counterpart, the IGCA—the Industrial Gas Cleaning Association—currently having 11 members.

The IGCI has been invited to appear at regulatory hearings, to present expert testimony on the performance capabilities of the gas cleaning industry. Typically, such testimony might involve the time span required for design, bidding, purchase, delivery, erection, start-up, and test on retrofit control installations in existing plants.

IGCI president Wright
noting annual highlights

Name dropping

John Thomas (American Air Filter) is senior U.S. Delegate on ISO TC-142, International Standards Organization (Geneva, Switzerland) technical committee 142. Thomas says, "This committee is working on standardization in the field of dust collectors and purifiers, including, in particular, their classification, the methods of measuring their characteristics and the sampling and analysis methods for dust, droplets and gas in gaseous flows prior to their release to the atmosphere."

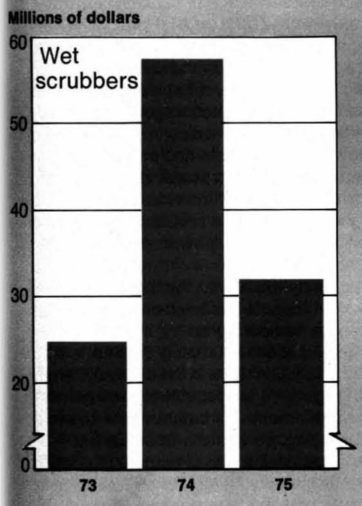
Also, the U.S. and U.S.S.R. exchange delegations on control of pollution from thermal power plants jointly sponsored a symposium on improved fine particle control in the Soviet Union in May. The U.S. delegation continues to be chaired by Harold L. Falkenberry, chief, Power Research Staff, TVA. Wheelabrator-Frye's Frank Culhane and Research-Cottrell's Dr. Norman W. Frisch were members of the U.S. delegation.

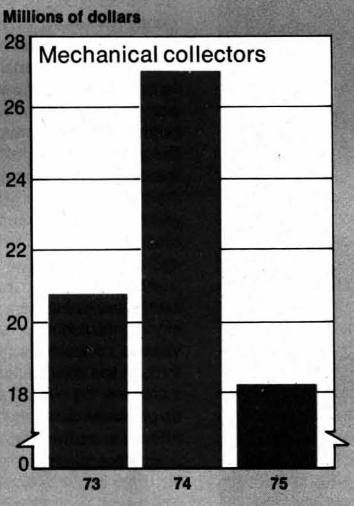
Culhane was co-author with James Turner of Industrial Environmental Research Laboratory, EPA, of a paper on fabric filters as applied to particulate control from power plant stack gases. Dr. Frisch was co-author with Alan B. Walker (also Research-Cottrell) of a paper on U.S. design and operating experiences with "hot side" electro-static precipitators in power plant applications. Frisch says, "hot side precipitators usually avoid the high resistivity problems frequently associated with low sulphur fuels in cold side precipitators."

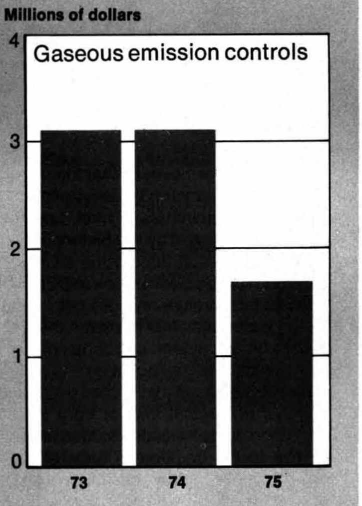
What industry seeks

Industries are looking for energy conservation methods and ways to use less energy not only for their manufacturing operations, but for their air pollution control systems as well.

Thirty years ago, the major portion of Portland Cement manufacturing capacity utilized the wet process. In the more recent past, especially with increasing energy costs, the cement industry has been converting to dry process production. Improved technology has reduced the fuel required per barrel of cement from 1 500 000 to less than 600 000 Btu. Some 85% of the U.S.S.R. cement production capacity currently uses the wet process, and studies are underway to convert a substantial block of this capacity to dry process methods also. SSM







FEATURE

How to put waste heat to work

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The mutual evolution of ecological assessment, engineering designs, and regulatory considerations is making "thermal pollution" manageable. However, certain impacts associated with the cooling process remain as important technical and social issues.

In 1972, Arthur Levin of Battelle Memorial Institute, and his associates (*ES&T*, March 1972, p 224) reviewed ecological effects of thermal discharges to aquatic systems. While many of the points they raised are still appropriate, a number of developments have changed the perspective of concern for the impacts of power plant cooling. Among these recent developments are

- completion of several large-scale field investigations of thermal effluents in which intake problems became apparent
- advances by the engineering profession in both predicting thermal discharge patterns and in designing outfalls that minimize zone of extreme temperatures
- publication of a National Academy of Science report on water quality criteria, including temperature
- passage of the 1972 water pollution control amendments with their emphasis on closed-cycle cooling
- the energy crisis, which has stimulated uses for waste heat
- a general maturing of the field of environmental impact assessment to the point that it has begun to consider risks of significant population or ecosystem damage, rather than concentrating on effects to individual organisms.

Heat

Previously, it was believed that the principal impact of power plant cooling systems on the environment came from the discharge of large quantities of heat. Laymen and professionals alike were conditioned by the history of water pollution control efforts to consider principally the substance(s) that emanated from the discharge pipe. For power plants this "substance" was heat, felt as temperature changes both in the cooling water itself and in the water body that receives the effluent. Heat was proclaimed to be a pollutant, and demands arose from many quarters to control "thermal pollution".

It is now understood that heated discharge is only one source of potential ecological impact from the cooling system of a power station. It is also understood that the principal engineering alternative to the traditional "once-through" cooling system, namely the cooling tower, has its own potential for influencing the environment. The area of impact may be in the terrestrial as well as in the aquatic environment. What is therefore necessary is an integrated approach to assessing ecological impacts and alternative engineering solutions for the overall power plant cooling system.

One reason for the early emphasis on temperature changes in aquatic ecosystems was the circumstance that most early studies of thermal effluents were conducted on small freshwater rivers in which temperatures remained high after effluent release. There, thermal effects were often dramatic and usually detrimental to the preferred ecosystem. For example, in the late 1950's, hot effluents from the Martin's Creek Power Plant (Pa.), studied by F. J. Trembley and others at Lehigh University, made striking changes in the composition of bottom fauna and attached algae of shallow riffles in summer, and attracted and killed many fish in the discharge canal in cooler months. Ruth Patrick, of the Philadelphia Academy of Natural Sciences, and her co-workers studied several small river locations, including the U.S. Energy Research and Development Administration's Savannah River Plant where production reactors heated the small streams of the swampy terrain to very high levels.

Studies of power plants (*ES&T*, March 1972, p 225) on large river systems and lakes, however, often failed to show such dramatic changes. Also, engineering designs that dispersed thermal effluents rapidly came into practice, and expanding knowledge of thermal effects provided boundary conditions for power plant designers to meet. This is not to say, however, that additional thermal data are not needed. On the contrary, there is still an inadequate understanding of behavioral responses to temperature, synergistic effects with toxicants, and long-term ecosystem effects of changed temperatures. Species-specific data on thermal responses, recognized as important for predicting impacts or setting limits for plant designs, are also lacking.

Entrainment and impingement

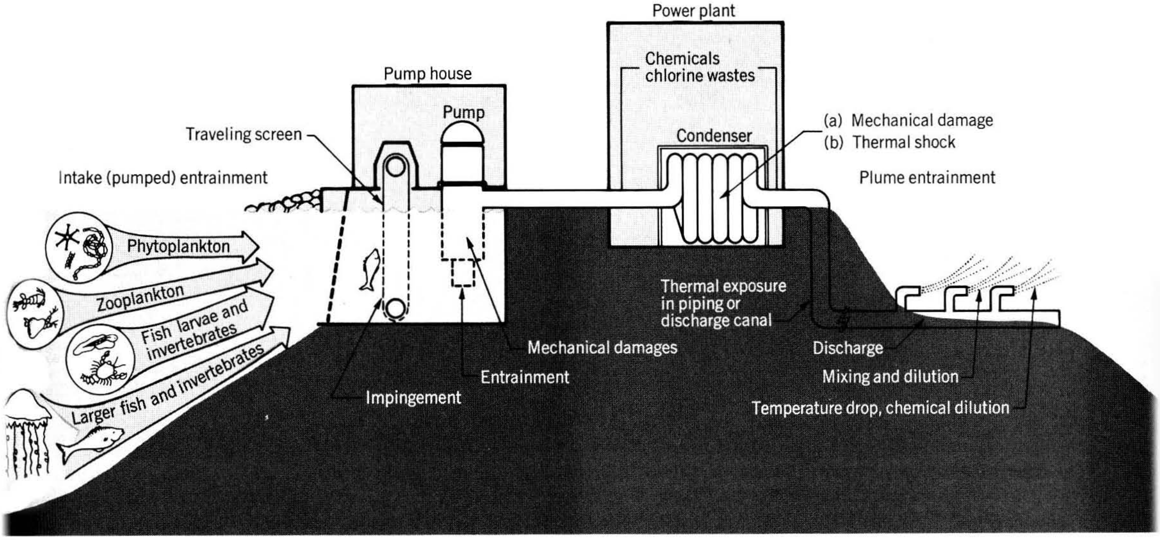
More recently, researchers began to notice effects related to the passage of water through the power plant system, rather than ecological damages at points of thermal discharge. Large fish and invertebrates were often impinged and killed on intake screens that had been designed to keep debris out of the condenser tubes. Small organisms, particularly larval stages of fish, were mutilated or thermally killed during their transit (entrainment) through pumps, heat exchange condensers, and piping. Whether screened out or entrained with the cooling water, organisms at the intake often seemed to fare worse than organisms at the discharge which had never been through the system.

The change in attention from thermal discharge to cooling water intake accompanied expansion of the utility industry to estuarine siting of steam electric stations. Small freshwater rivers generally have only limited amounts of planktonic organisms that would be susceptible to entrainment. Estuaries, however, are important spawning grounds and nursery areas for large numbers of aquatic species. Here, recirculating hydraulic patterns of fresh and salt water have encouraged evolution of drifting larvae. These drifting larvae cannot discriminate between the patterns of water flow that recirculate and nourish them in the estuary and those that draw them into power station intakes. As power stations grow both in size of individual units and in numbers of units on a given estuary, the probability increases that a larval fish will be entrained in a power station cooling system before it leaves the estuary.

An unfortunate result of early fixation on the thermal effluent component of cooling water impacts has been engineering designs that reduce discharge temperatures by increasing the volume of water pumped. Additional pumping volume, either through the condensers or as dilution flows in the discharge area, increases the numbers of organisms susceptible to impingement or physical damage of entrainment. On balance, the thermal effects are often less damaging, particularly in estuaries.

Ecological changes associated with the structures of cooling systems became apparent as intakes began to be looked at in detail and as discharge schemes made increasing use of elaborate effluent diffusers. Artificial shelters were created that attracted new species assemblages. Often, the structures at in-

Power plant cooling system's pollution sources



takes attracted fish and entrapped them in intake areas from which there could be no escape other than impingement on screens.

Plant structures also created some markedly different habitat conditions. For example, rock rip-rap and concrete changed areas of sandy beaches along lakes or the ocean into new habitats with unknown consequences for the ecosystem.

In addition to heat, chlorine is released in cooling waters either as slugs at intervals or as continuous additions at low levels. The chlorine is purposely added to reduce accumulations of biological slime that impairs heat transfer efficiency on condenser tubes. Larger fouling organisms, especially in marine waters, are prevented by chlorine from attaching to pumps and piping. The biocidal activity that is intended for specific target organisms necessarily acts on non-target organisms as well. Many of the ecological damages once ascribed to heat are now being more properly traced to chlorination.

Cooling towers

Cooling towers, as the principal non-aquatic alternative to "thermal pollution", have also come under scrutiny as sources of ecological damages. Despite their characterization as "closed cycle" systems, owing to the recycling of cooling water, these systems do discharge wastes to the environment.

Mechanical draft towers (in which a fan circulates air among water-covered wooden slats to speed evaporative cooling) blow a mist of cooling water droplets into the air as "drift". Also, all towers must release their cooling water to the environment as "blowdown" after several cycles through the system, in order to prevent excess buildup of salts as water is evaporated. Both of these releases involve chemicals that are added to the cooling water as corrosion inhibitors (such as chromates and organophosphate complexes) and biocides (principally chlorine). Terrestrial vegetation may suffer from airborne drift chemicals; aquatic organisms may received toxic quantities of blowdown chemicals. Organophosphorus compounds in blowdown can amount to significant inputs of phosphorus to waters already showing symptoms of advanced eutrophication caused by phosphorus enrichment.

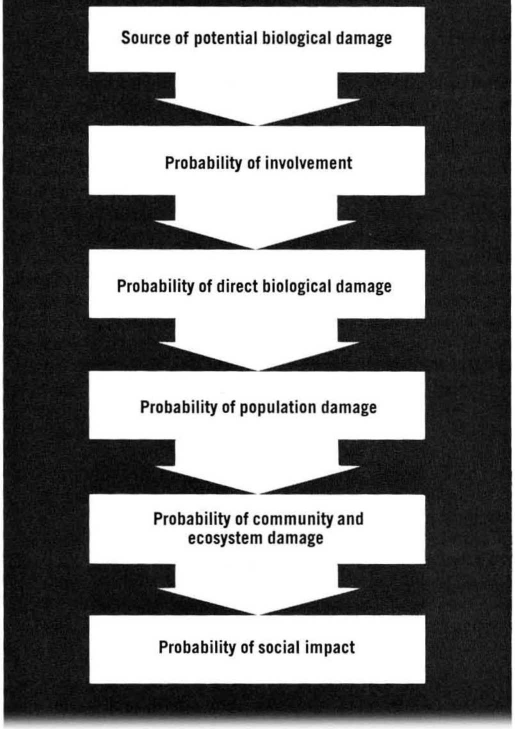
Makeup water to compensate for evaporation and blowdown in cooling towers must be drawn from some water source at which problems of entrainment and impingement could arise; however, volumes are usually less than 10% of those required for open-cycle systems. Fogging by cooling tower plumes may cause safety hazards when towers are inappropriately located near airports or roads. Thus, cooling towers are not simple answers to pollution problems, but are engineering schemes with potential impacts of their own that should be compared with impacts from open-cycle systems.

Probability of risk *vs* proof of effect

Current perspectives on power plant impacts are increasingly aimed at assessing probabilities of risk for aquatic populations, communities, and ecosystems. The field of pollution control has matured beyond the phase of simply demonstrating that there can be effects of potential pollutants on the organisms of the biosphere. It has entered the more difficult and demanding phase

FIGURE I

Impact assessment steps



Productive conservation. *Tomatoes and beans thrive in this greenhouse warmed by waste heat*

of assessing the probabilities of risk associated with having particular human developments on particular types of water bodies.

This maturation of the assessment process intensifies the need for scientific and social evaluations and minimizes applicability of across-the-board, numerical limits imposed by national regulatory agencies. The requirement of the National Environmental Policy Act of 1969 that environmental impact assessment be conducted for major federal actions was evidence of this maturation. This is one reason why the National Academy of Sciences/National Academy of Engineering report, "Water Quality Criteria 1972", emphasized that it was presenting a method for analysis of thermal effects on aquatic life, not a set of rigid numerical guidelines.

A conceptual framework for impact analyses of power stations on aquatic life, which encompasses several stages and requires expertise in many disciplines, has evolved (Figure 1). Determining the probability of direct biological damage is merely one step leading toward assessment of risk to the ecosystem. The analysis must begin with careful attention to all sources of potential ecological damage (or change) from the facility, both in operating and construction phases. Then, information on the distribution and abundance of organisms in the ecosystem must be coupled with hydrologic and hydraulic assessments to determine the likelihood that key organisms or life stages will come in contact with the source of potential damage.

Once damages to the organisms are estimated, they must be translated into changes in population dynamics of the key species, particularly as yields to fisheries or possible declines to lower equilibrium levels or to extinction are concerned. At community and ecosystem levels, risks to normal structure and function, for example, change in diversity and types of species, and functional aspects such as energy flow and nutrient cycling are sought. Often, computer modeling is the best approach to examining population, community, and ecosystem effects, although such techniques are in their infancy. The assessment of the probability for social impact from any ecological changes is the final step.

Local conditions of the receiving systems are now seen to be as important to assessing probability of risk as are the general data on the direct biological effects of human activity. This fact is at variance with the long-held philosophy that standards for pollutants can be established for the nation as a whole, or even for entire states, based on representative scientific literature. To consider only the potential effect of an effluent or structure without looking at its realistic interactions with the receiving system is to see only half the story. Regulatory restrictions developed through analyses of probabilities of risk will necessarily be *localized* restrictions, tailored to the particular receiving system (water body, regional air mass, and the like).

Assessment of risk, however, implies that one has some clear notion of what would be put at risk. One must clearly state the object or property believed to be at risk, and make social decisions regarding objectives for that object or property. Thus, chronic effects of power stations on an estuary can hardly be evaluated against vague notions of the "proper functioning" of the estuary ecosystem. On the other hand, if one defines "proper functioning" to mean, for example, continued yield of high numbers of striped bass to the commercial and sports fisheries, then there are clear objectives against which to measure the significance of any direct effects at the power station. Certainly, the objectives chosen would need the backing of either scientific justification or social desire.

Such objectives vary from location to location across the country. Enhancement of largemouth bass populations in rivers and reservoirs, for example, is seen as a prime goal in the "bass country" of the American southeast; yet this species is considered an undesirable competitor with salmon in the Pacific Northwest. As the objectives differ, so do the assessments of risk and the restrictions that are selected to minimize risk in a particular location.

While there now seem to be clear objectives for environmental impact assessments of power plant cooling systems, one must concede that present environmental knowledge is inadequate for a comprehensive assessment. Knowledge of direct biological effects exceeds present understanding of what these combined effects mean to populations. The most comprehensive models of population dynamics of important species falter when interactions among species are questioned.

"Ecosystem Analysis" is a new framework for determining ecosystem-level impacts (which received deserved attention in the intensive International Biological Program activities of the past 5 years), but ecosystem understanding has yet to advance to where useful predictions can be made for installations such as power stations. Impact assessment can proceed only as far as the understanding of environmental systems is advanced through research and analysis. To enhance this understanding, much-needed studies are presently being funded by the Energy Research and Development Administration, the Nuclear Regulatory Commission, the Electric Power Research Institute, the Environmental Protection Agency, and many electric utilities.

Waste heat management

There is a growing desire to put waste heat to use rather than to disperse it to the environment in ever more costly cooling devices. Some of these uses are ecological. It seems clear to most people that society must learn to conserve energy; the great national debate now is over how to conserve. Rather than regarding conservation according to the dictionary definition (to keep from being damaged, lost, or wasted), most people think of conservation as reduction in energy use. Lights are turned off, car pools are formed, and so on. Such forms of *reductive energy conservation* may momentarily slow energy use, but the long-term trend will still be upward. However, a better answer may lie in *productive energy conservation*, in which degraded energy is put to further productive uses. For instance, heat that is reused does not have to be generated with additional fuel.

A principle that is emerging from ecosystem research is that complex mature ecosystems have efficient devices for keeping energy within the realm of productivity with only a gradual loss as heat. While the initial conversion of solar energy to organic molecules is not very efficient, elaborate biochemical systems in organisms and diverse species assemblages in ecosystems effectively utilize a "low grade", dispersed radiant energy source and keep converted energy at work as long as possible. Human society could emulate the efficiency. It is encouraging to see analyses of net energy use being developed; there could be a start toward developing energy-efficient social systems.

Productive uses of waste heat range from moderate management of thermal discharges to complete engineering control of the flow of heat for industrial uses or building heating. In certain areas, experimental or production greenhouses are making use of waste heat. The most often discussed ecological uses are in aquaculture where temperature control at near-optimum growth temperatures for the cultured species can markedly increase protein output, as compared to uncontrolled culture systems. Species that require years to grow to market size in nature can be harvested within one year under thermal aquaculture. For example, catfish have been successfully grown in thermal culture systems at the Tennessee Valley Authority's Gallatin Steam plant in Tennessee, and by a commercial grower at a power station in Nebraska. Oysters are cultivated in warm discharge waters of the Long Island Lighting Company's Northport plant. Obtaining sufficient food for rapid growth rates, the near-impossibility of using significant quantities of the nation's waste heat for such purposes, and the institutional problems of linking food producers with electric utility companies seem to be the main discouraging notes for such enterprises.

A promising "use" for waste heat is in development of multipurpose cooling reservoirs. Wherever sufficient land is available, cooling reservoirs offer distinct advantages in costs and social benefits over cooling towers. Power plant cooling waters appear to enhance recreational fishing on small reservoirs by providing longer growing seasons for game fish, by concentrating fish and fishermen in discharge areas in cooler months, when catch rates are improved, and by improving the ratio of game fish to non-game fish. Whether the effect is caused by added heat *per se*, or by induced current patterns that prevent summer deoxygenation near the bottom has not been settled; the benefits appear real, however.

The key to a successful multipurpose reservoir appears to be in designing and managing a nearly closed reservoir system that incorporates the needs of the key species (for example, largemouth bass) as well as those of the power station. Indiscriminate discharge of heated waters to natural systems is replaced by an integrated, managed system designed to provide maximum recreational opportunity as well as optimum heat dissipation for the power plant. Many such man-made systems are already operating; the researcher's task is to determine why they function well, so that design criteria can be established for new ones.

Verification of predictions

There is an increasing pragmatism concerning verification of dire predictions of thermal and other power plant effects. For about 20 years, researchers, regulators, and lay environmentalists have hypothesized a long list of possible ecological consequences of cooling water use. It seems appropriate now to determine which of these hypothetical consequences occur and which present any significant risk to populations, ecosystems or social values.

Field research is at a stage at which reasonably detailed comparisons between hypotheses and observed results at many power stations across North America and in Europe should be able to be made. Environmental impact statements for nuclear power plants, prepared since 1971 by the U.S. Atomic Energy Commission's Office of Regulation (now the Nuclear Regulatory Commission), are massive sets of hypotheses that are now being evaluated, based on monitoring data that are becoming available. Many suspected long-term effects can be sought at smaller fossil-fueled power stations that have operated for many years. In the tradition of the scientific method, ecologists should be able to view objectively both the hypotheses and the results, and to arrive at conclusions that can genuinely aid the next generation of power plant designs.

An appropriate guideline for the future is that there is some environmental impact from anything done. An engineering system as complex as power station cooling is bound to have many sources of potential environmental change associated with it. For years, only the thermal component was a matter of concern. The perspective has now broadened with regard to the open-cycle system, but there is a trend toward similar shortsightedness concerning potential impacts from cooling towers. Instead of searches for a panacea, a careful analysis of the relative impacts of alternative cooling schemes at a chosen location is needed, as well as more careful selection of sites that will present minimal environmental complications. Environmental impact itself should also be measured against other goals and needs of society.

There are uses of waste heat from power stations that can turn part of the environmental problem into a social benefit. It is ironic that increasingly complex devices are designed for dumping waste heat into the atmosphere while the world suffers an energy shortage. Multipurpose cooling lakes, thermal aquaculture, and greenhouse heating offer possibilities of enhancing ecological productivity in ways desirable to man. Disposal of waste heat from electricity generation should be integrated with energy requirements of the region. In many cases, overall energy efficiency might be improved if there were to be less efficiency in electricity production, leaving a higher temperature discharge more suitable for other uses.

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Coordinated by JJ

Physical, psychological, and economic factors contribute to the problems encountered when . . .

Cities spread to once-remote airports

When any aircraft accident occurs it is a tragedy. But as has happened all too frequently in recent years, when an aircraft, shortly before landing or immediately after takeoff, crashes into a densely populated business or residential area, it is more than a tragedy. Beyond the loss of life and property, these accidents have another meaning. They are manifestations of the crisis around the airport—a crisis that military, civilian and commercial aviation face.

Since December 1903, when the Wright brothers made powered, controlled flight a reality, aviation has progressed from being a mere curiosity to, at present, being an important part of the daily life of nearly everyone in the U.S. Everyday commodities, as well as exotic equipment such as the rockets used to hurl our astronauts and planetary exploration vehicles into space, are carried routinely across the nation and around the world by air. In 1975 almost 191 000 000 passengers were carried by airlines within the U.S.

The airport's impact

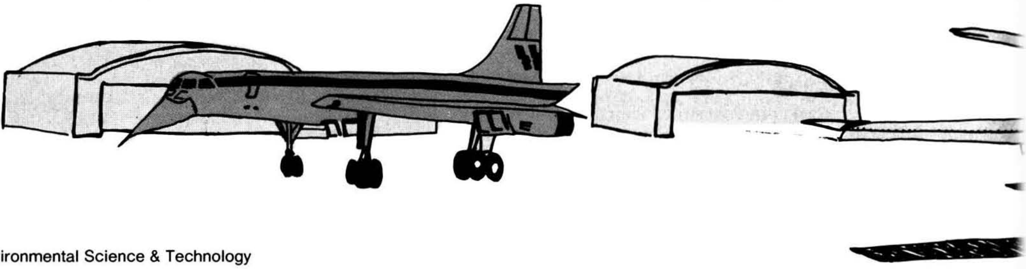
Major cities and even some states depend on the airlines for their economic livelihood. Hawaii had over 2 600 000 tourists who spent over $1 billion in 1974. Tourism is the biggest industry in Hawaii, topping defense spending, pineapples and sugar.

Las Vegas, a city with a population of only 334 000 people, annually draws over 8 600 000 tourists who spend and gamble away more than $1.88 billion. Name a major city in the U.S.: New York; Reno; Niagara Falls; Miami Beach; Chicago; Los Angeles; New Orleans; San Franscisco, San Diego; and tourism, conventions, and businesses that are major economic factors in sustaining its prosperity are nurtured by a steady flow of nonresidents in and out of the city limits. The heart that pumps this economic lifeblood of people and money is aviation.

Yet, the very technology that has produced faster, bigger, and more efficient aircraft capable of moving up to 400 passengers from New York to Miami Beach in less than three hours has also spawned the crisis around the airport.

As the aircraft industry has grown more complex and has expanded in size and services to meet the demands of our business and leisure economy, the size of airports and the ancillary industries associated with them have turned the areas around major air terminals into industrial complexes. Simultaneously, businesses that rely on air transportation have gravitated to the airport environs to reduce costs in transportation of goods, as well as the time required to get goods to distributors and consumers.

With major airports now industrial centers employing, directly or indirectly, some tens of thousands of people, it is only natural that these individuals purchase or rent homes as close to their place of work as possible. This creates a need for shopping centers, schools, recreation facilities, churches, and all the other necessities of a residential community. These community facilities in turn increase the population dwelling near the airport as the people who provide these services move into the area to be near their place of business. The services and facilities, new housing development, and modern highways and other transportation modes linking the airport to the metropolitan center, increase the property values of land near the modern airport complex. This increases its desirability as a residential area for people who have no connection with the airport. Thus the airport, once a remote facility beyond the edge of town, becomes an integral part of the city itself. When all these factors are combined—the bigger aircraft with larger and noisier engines that emit untold pollutants into the air and that fly more frequently, and the encroachment of cities up to and in some cases past the airport—the crisis around the airport occurs. Accidents, noise complaints, environmental questions, suits and court tests then



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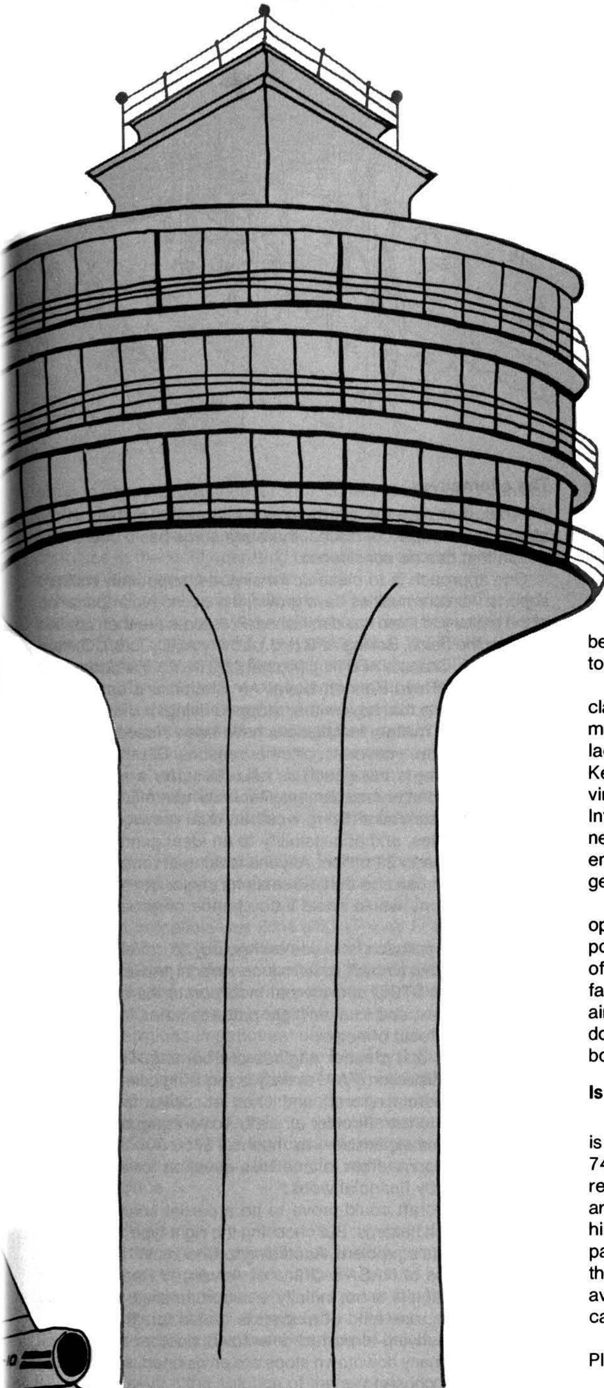


become common. This crisis stage has been reached in the U.S. today.

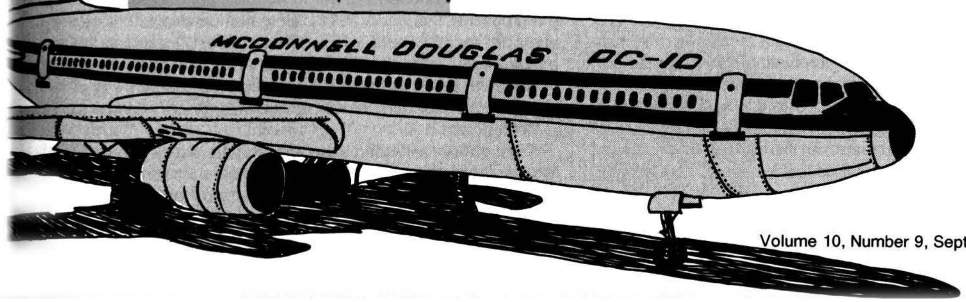
John F. Kennedy International Airport in New York City is a classic example. Created some 16 years ago from the muck and marshes of Jamaica Bay, in a sparsely populated area that lacked easy accessibility by road or any other means, today Kennedy Airport is surrounded by housing developments on virtually every piece of land within 20 mi in any direction. Dulles International Airport, which serves Washington, D.C., is witnessing the same type of growth. To a greater or lesser degree, encroachment is taking place at almost every commercial, general, or military aviation facility in the U.S.

As growth around an airport occurs, dissatisfaction with airport operations arises. Complaints about noise, pollution, and crash potential are received by airport, community, state and federal officials. In most instances, the airport was there first, but that fact makes little impression on its new neighbors who view the airport's activities as an invasion of their privacy. These people don't want flying to stop; they just want it to stop in their neighborhood.

Is the crisis perceived?

For many Americans the idea of an airport crisis is unreal. It is difficult for the traveler sitting in the cocktail lounge of a Boeing 747, or a pilot flying a U.S. Air Force (USAF) military craft to realize that they are involved in and contributing to the crisis around the airport. Similarly, it is difficult for a recent retiree and his wife who are moving into a home directly under the flight pattern of the USAF's largest fighter base to comprehend that they are part of a national problem that extends well beyond the aviation industry. But they and literally millions of other Americans are intimately and inexorably part of the problem.

Nevertheless, according to Gary D. Vest of the Environment Planning Division, Directorate of Engineering and Services,



Headquarters USAF, "Airports and their impacts are real. They are here to stay. However, there exist serious conflicts between many airports and the land areas in their environs." That conflict has several ramifications.

The EPA considers the problem of noise from airport operations to be quite serious and growing more so every day. The agency estimates that there are 16 million people in America living or working in and near airports who are affected by aircraft noise. In 10 yr, the EPA predicts that this figure will grow to 24 million people. Harry Nelson, a medical writer for the *Los Angeles Times,* states: "There is good reason to believe that hundreds of thousands, perhaps millions, of Americans are slowly becoming partially deaf—painlessly and usually without an awareness of what is happening to them." This loss he attributes to the rising noise level of the American environment, and for people in and near airports he considers jet aircraft to be prime contributors to high noise levels.

Nelson points to physical and mental effects from exposure to noise levels such as the 100 dB generated by a jet transport at 1000 ft. He cites studies from Europe and from medical schools in Southern California that show that increased diastolic blood pressure occurs in men exposed to noise near 100 dB. If the exposure is sustained, the blood pressure does not return to normal, even with the aid of drugs, when the individual is removed from the noisy environment. Couple noise with the pollutants emitted to the air from jet engines and the physical effects of aviation on the well-being of millions of Americans become evident.

Economic considerations

But there is more to this crisis than the physical and psychological effects on people. There is a decidedly economic factor too. Land around airports is valuable. The people who own it, in most instances, wish to subdivide it for residential use.

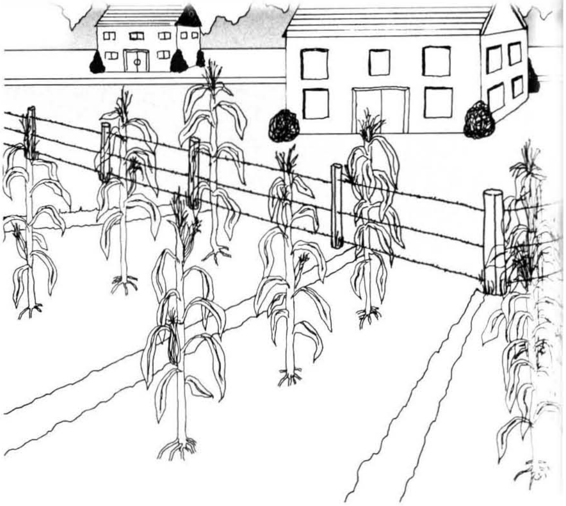
A lawsuit filed by a landowner against the county board of supervisors in Maricopa County (Arizona) Superior Court highlights the problem of regulating land use around airports. In this case the supervisors, following the recommendation of the county planning and zoning commission, refused the property owner's request to subdivide his land into residential lots because it was less than two miles from the runways of Luke AFB, the USAF's main F-4 Phantom jet fighter training facility. The supervisors felt that the development would expose residents to dangers from possible crashes and the noise of aircraft whose flight patterns would pass near or over the homes in the proposed development.

According to newspaper reports, the lawyer for the landowner saw the action as denying his client a chance for a fair return on his investment: "If we meet all legal requirements, we have a right to legally subdivide in accordance with regulations." The Arizona courts agreed. With no county or state statutes adequately covering the matter of land-use planning around airports, this suit succeeded, not because the board of supervisors was doing something wrong, but because it lacked legal authority to protect the people as well as the airport.

How much money was involved? As farmland, the property was worth $18 000. Subdivided, the price tag jumped to $3.6 million.

At one time, Los Angeles International Airport was the defendant in noise damage suits totaling $5 billion. Prior to one trial, which cost the airport $365 700, the city bought some 34 homes for $1.8 million.

One cannot shrug off figures like these by simply saying: "The property owners deserve it; the government should pay or build the airports someplace else." It takes only a moment's reflection to realize that we are running out of available land around our cities, that it costs too many billions of dollars to construct first-rate airports, and that we cannot afford to keep threatening the health of people and then paying them damages. Conversely, aviation is not going to disappear from the transportation scene. Along with the automobile, aviation is the basis for our mobile society.



The alternatives

What, then, are the alternatives? Although the crisis at the airport is a complex of issues, there are some basic courses of action that can be considered.

One approach is to close down airports, especially military airports. As communities have grown, the economic importance of the military to them has diminished. Pressures are then applied to close the fields. Bolling AFB (Md.), Lowry AFB (Colo.), Oxnard AFB (Calif.), Chanute AFB (Ill.), Mitchel AFB (N.Y.), Hanscom AFB (Mass.), and Floyd Bennett Naval Air Station are among the military airports that have either stopped flying or closed down entirely. Many military installations have been closed for sound national defense, economic, or other reasons. But there is little logic in allowing a base such as Luke to suffer a similar fate because of urban encroachment. Replacement of Luke, which has perfect year-round flying weather, dual runways, modern support facilities, and accessibility to an ideal gunnery range, would run close to $1 billion. Anyone looking at recent defense appropriations can see that requests for major construction of new installations would stand little chance of acceptance by Congress.

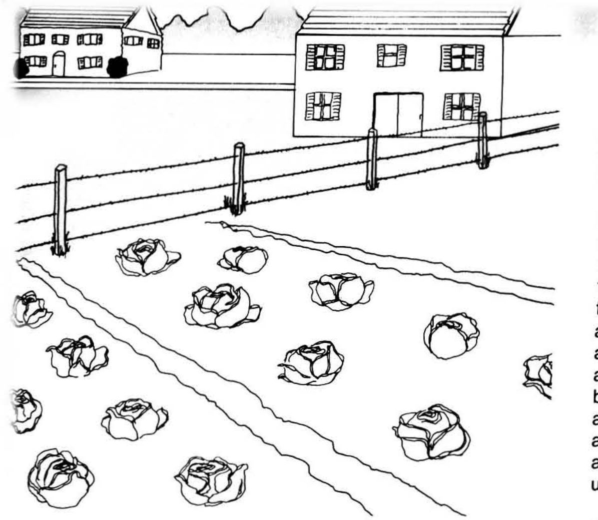
A second approach is to use technology to develop quieter and less-polluting aircraft, to introduce vertical and short takeoff and landing (V/STOL) aircraft that incorporate the quieter and cleaner engines, and to alter flight patterns so as to minimize the harmful effects of noise.

The quieter and cleaner engines are coming. The Federal Aviation Administration (FAA) already is requiring quieter engines on new commercial aircraft, and it has let contracts for design modifications to retrofit older aircraft. To re-equip one Boeing 707, however, is expensive—as much as $750 000. Where that money would come from is a serious question for an industry already beset by financial woes.

V/STOL aircraft could prove to be a partial solution to the noise and crash hazards. But choosing the right type of V/STOL aircraft presents a problem. According to Charles W. Harper and Albert J. Evans of NASA's Office of Advanced Research and Technology, "If it is to be, initially, a suburban-area-to-central-airport system, one kind of aircraft is called for. If it is to be suburban-or-outlying-airport-to-downtown, another type would be chosen. If many downtown stops are envisioned, still another type might be chosen."

To be effective, the V/STOL aircraft must provide more services to more people while simultaneously reducing noise, pollution, and crash hazards. Harper and Evans put it this way: "It will take a well coordinated and decisive effort by city planners, aircraft designers, airway systems designers and operators . . .to succeed."

Flight-pattern alteration is another way to reduce noise. While this can be extremely effective, it can also present problems, particularly for military aviation, which trains large numbers of



pilots in high-performance aircraft. Safety is the prime consideration. While take-off power may be curtailed, a steeper glide path used, or a segmented approach tried, these are all compromises in the ideal operating mode of the aircraft, and could produce fatal results in an emergency.

Nevertheless, all possibilities should be considered. The FAA is currently working on a two-segment approach that would keep aircraft higher longer as they prepare to land. The FAA has also been studying lower wing flap and reduced engine thrust combinations. The airlines are continuing similar tests.

A third alternative is to adopt planning and zoning legislation that will prevent encroachment upon airports. This, however, is a very sensitive subject. Great pressures can be brought to bear on city, county, state, and federal government by business, industry, and landowners when somebody starts telling them what they can or cannot do with their land and expansion plans.

Despite this, there is still hope. The Air Force has devised a tool that can be used by communities in land-use planning around airports, whether military or civilian. The tool is called the Air Installation Compatible Use Zone (AICUZ) (see *ES&T,* November 1975, p 1025). AICUZ synthesizes information on flight and accident patterns of aircraft operating from an airport and noise generated by the aircraft with possible land uses around the airport. It also provides degrees of noise attenuation achievable through alterations in structural design and the choice of construction materials. With the data furnished by AICUZ, and proper legislation on the books to allow zoning around an airport, a planning and zoning commission or county board of supervisors can make appropriate decisions—decisions that will allow the airport to operate and the landowner to receive a fair return on his land while still assuring the health, welfare, and safety of the entire populace.

Summing up

None of these three approaches is truly going to solve the crisis around the airport. Realistically, a total solution to the situation is probably impossible. Yet some things can be done to reduce the problem considerably. Perhaps a program is needed that incorporates some aspects of the second and third approaches.

As Vest says, "the solution of the airport . . . problem must begin with the recognition that there is, in fact, a problem and that if it is not resolved the results will be unacceptable." Gaining recognition of the problem around military airfields is more difficult because, in many instances, these fields do not represent a major factor in the community. The problem will intensify as the economic impact of these airfields on local communities continues to decline and the transient military members of the communities are unable to wield the political power of permanent residents.

If the hearing and psychic damages faced by 16 million Americans, the billions of dollars in lawsuits already settled or pending, and the costs of building new airports, whether military or civilian, do not represent a recognizable problem, then there is a communication and comprehension gap.

The first thing that must be done is to educate people. The Departments of Defense, Interior, Transportation, Health, Education and Welfare, the FAA, the ICC, and any other agency involved in aviation at the national level, should combine and intensify efforts to obtain national legislation that will require states to enact laws that mandate proper land-use planning around airports or requiring that in the absence of such laws they follow a minimum federal statute. Similar action should be undertaken at state, county, and city level. In addition, at the local level, building codes should be sought that require appropriate and adequate noise attenuation, whether the source of noise is an airport or a toy factory. Here the catalyst should be the aviation and business communities, the people who own, operate, and use aviation on a daily basis.

Where inappropriate zoning has been made, government should subsidize noise attenuation, redevelopment, or even outright purchase of the structures, as was done in Los Angeles. Although initially this might be costly, in the long run it could be considerably cheaper than the cost of lives and settlements of lawsuits that follow accidents. Subsidization could save many airports that are now restricted in their operations or face closing, thus saving the construction costs of new airports while providing convenient facilities for air travel within the city.

At the same time, every technological option, including V/STOL aircraft, should be explored. Similarly, flight patterns and procedures need to be carefully examined to see what, within the limits of safe operation, can be done to reduce noise.

Research efforts to produce quieter and cleaner-burning engines should be further underwritten, either directly or through tax advantages. At the same time, as quieter and more efficient engines are developed, the government should back low-interest loans or other means of subsidizing the costs of retrofitting existing aircraft.

The solution to the crisis around the airport requires a multifaceted, multilevel approach involving the total commitment of many government agencies and the entire aviation community. It is not a problem that will go away or be brought under control without hard work and much conciliation.

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The views expressed in this article are solely those of the author and are not those of the Department of Defense or the U.S. Air Force.

This feature is condensed from an article that first appeared in March–April 1975 issue of *Air University Review.*

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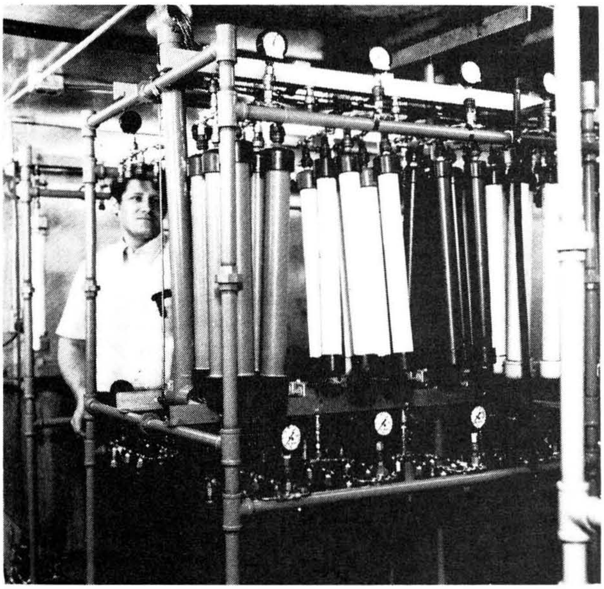

CURRENT RESEARCH

Atomic Absorption and Optical Emission Analysis of NASN Atmospheric Particulate Samples for Lead

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■ Lead analyses were performed on 945 quarterly composited particulate samples collected in 1970 by the National Air Surveillance Network by atomic absorption and spark excited optical emission spectroscopy. Duplicate analyses by atomic absorption (283.3-nm line) of 203 samples gave a pooled precision of 3.4%, RSD, with a detection limit of 0.50 μg/ml (0.10 μg/m^3). Duplicate optical emission (220.4-nm line) analyses of 800 samples gave a pooled precision of 11%, RSD, with a 9.6-μg/ml (0.15 μg/m^3) detection limit. Spike recovery data were 93 ± 9% for atomic absorption and 102 ± 8% for optical emission data. Analysis of different portions of the same filters gave no significant difference by either method. The lead blank value for glass fiber filters was approximately 1 μg/in.^{2}. For 795 samples run by both methods, the most frequently occurring difference in concentration was 8% which was statistically significant at the 99% confidence level. The emission data were higher than the atomic absorption data. No evidence was found for interferences on the 283.3-nm atomic absorption line. Times required for sample preparation and analysis were 1.2–1.4 man-hours per sample.

The determination of lead in atmospheric particulate samples by atomic absorption spectroscopy was apparently first accomplished by Chakrabarti et al. (*1*) in 1965. West and coworkers suggested the use of a hydrogen–oxygen flame and the 217-nm analysis line with the addition of EDTA to the liquid sample to reduce interferences. Further investigations with the 217-nm line by Burnham et al. (*2*) using 38 samples collected in the Chicago and Cook County area indicated the necessity of using the standard addition technique to overcome matrix effects. Later work by Burnham et al. (*3*) showed that the 283.3-nm line gave less noise and baseline shift than the 217-nm line. However, differences of up to 66% were obtained with either line when comparing standard addition and regular calibration data.

A solvent extraction procedure was suggested by Sachdev and West (*4*) in 1970 to concentrate trace quantities of lead, making an accurate determination possible when using the 217-nm lead line and an air–acetylene flame. In 1970 particulate matter samples collected by the National Air Surveillance Network (NASN) were analyzed with an air–acetylene flame at the 217-nm line by Thompson et al. (*5*). They found that the matrix effect could be overcome by keeping the dissolved solids content less than 0.5% and did not use the standard addition technique. Hwang (*6*) in 1971 investigated particulate interferences on the 217-nm lead line and concluded that the standard addition technique was required to reduce sulfate and silicate interferences in the air–acetylene flame. Zdrojewski et al. (*7*) reported a very small interference on the 283.3-nm line due to the glass fiber filter extract. To our knowledge, no comparison of optical emission and atomic absorption data for lead in particulate matter for large numbers of samples has appeared in the literature.

Because lead is recognized as a toxic atmospheric pollutant, it is necessary to have a rapid, precise, and accurate method for its analysis. Whether or not the standard addition technique is actually required for atomic absorption analysis needs to be determined because of the additional amount of time imposed by the use of this method when handling large numbers of samples. The National Air Surveillance Network (NASN) consists of stations operating on a cooperative basis with local agencies at some 250 sites across the United States (*8*). This network serves in part to collect samples of air particulate pollutants on glass fiber filters. These samples are then analyzed to provide data on long-range trends of various air pollutants. The NASN particulate samples are routinely analyzed for some 24 trace elements including lead by optical emission spectroscopy. The 1000 NASN samples collected in 1970 were also analyzed by atomic absorption spectroscopy using the 283.3-nm line and an air–acetylene flame.

The data obtained from the 1970 samples will be presented in this paper. Precision, accuracy from spiked samples, time requirements, and possible interferences involved with the atomic absorption analysis will be discussed. This study is only concerned with a comparison of the optical emission and atomic absorption techniques. No attempt is made to evaluate the efficiency of the sampling medium.

Experimental

Sample Collection and Preparation. Particulate samples were collected at the NASN sites on previously weighed 8 × 10 in. glass fiber filters mounted on standard Hi Vol samplers. The sampling time was 24 h at an average flow rate of 100 m^3/h. The soiled filters, along with flow rate and sampling time data, were returned to EPA in North Carolina. They were reweighed to determine total particulate collected and then partially sectioned to distribute to the various analytical groups.

The total exposed filter area was 7 × 9 in. of the 8 × 10 in. filter. A pizza cutter and plastic template were used to cut 1-in. wide strips of appropriate lengths from the exposed filters to total 17.5 in.^{2} of exposed filter area per calendar quarter for each site. Each quarterly composite consisted of from five to seven strips, each taken from a different filter. The composited filter strips were ashed for 1 h at about 150 °C in a low-temperature asher (Tracerlab LTA 600) under an oxygen atmosphere. The asher rf power was 250 W, the chamber pressure was about 1 mm Hg, and the oxygen flow rate was 50 cm^3/min.

After being ashed, the composite filter strips were placed in a glass extraction thimble (23 mm id × 62 mm length) which

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was inserted into an extraction tube. The extraction tube was fitted into the top of a 125-ml Erlenmeyer flask through a 24/40 ground glass joint, and a reflux condenser was fitted to the top of the tube through a 34/45 joint. (Details of this apparatus are shown in ref. *5*.) The Erlenmeyer flask contained 40 ml of extracting acid containing indium and yttrium at levels so that subsequent concentration of the extract would yield final indium and yttrium levels of 200 μg/ml. The indium and yttrium were used as internal standards for the emission analysis. The extraction acid was a mixture of redistilled reagent grade 70% nitric acid (800 ml) and reagent grade hydrochloric acid (380 ml) made up to a total volume of 2 l. Both of the acids were tested for impurities by emission spectroscopy before use. The extraction unit was placed on a hot plate, and the acid refluxed over the filters for 3 h after the acid mixture attained its boiling point. An apparatus was used to support 32 extraction units per large hot plate.

After being refluxed, the extract was carefully concentrated to a volume of 1–2 ml and quantitatively transferred to a calibrated 15-ml glass centrifuge tube. Nitric acid, 70% (containing no indium or yttrium), was added up to a volume of 2.4 ml, and the solution was then made up to a volume of 11.1 ml with 1:10 diluted 70% nitric acid. The final solution contained about 20% nitric acid and 200 μg/ml indium and yttrium. This solution was centrifuged at 2000 rpm for 30 min to remove suspended material, and then a 5-ml aliquot was transferred to a nitric acid-cleaned polypropylene bottle for storage. The remaining portion of the sample extract was diluted by 1:12.5 with deionized water and retained for atomic absorption analysis. By use of a calibrated automatic dispensing pipet, 0.263 ml of 40% (w/V) lithium chloride solution containing 20% nitric acid and 200 μg/ml of indium and yttrium was added to the 5-ml aliquot before emission analysis.

Atomic Absorption Analysis. All of the 1970 NASN sample extracts were analyzed for lead on a Perkin-Elmer 403 atomic absorption spectrophotometer utilizing an automatic sample changer with teletype control. The background corrector was not used during these analyses. This arrangement furnished a punched paper tape output as well as providing a written record of the analyses. The 283.3-nm lead line was used with an oxidizing air–acetylene flame and 1-nm slitwidth which corresponds to a 0.7-nm effective bandpass. The samples were run in blocks of nine followed by a standard. Prior to sample analysis and after every 90 samples, the complete standard series covering the range 0.1–20 μg/ml was run. Working standards were prepared by dilution of certified standards with redistilled nitric acid so that each contained approximately 2% nitric acid and the appropriate lead level. As part of our quality control, 16 blank filters, 16 spiked filters, and 16 replicates (cut from different positions on the same filter) of composites were integrated with the regular samples. Some 203 solutions were reanalyzed at different times in the series of analyses to confirm that they contained 7 μg/ml or more of lead, which corresponds to a relatively high 1.4 μg/m^3 for an average air volume of 2500 m^3.

All initial data tapes were edited on a data handling system composed of a PDP-8/I digital computer, ASR-35 teletype, and high-speed paper tape reader and punch to remove tape entry errors such as mistyped sample numbers. These corrected tapes were used both to construct linear least-squares calibration curves and to process sample data. Blocks of standards and samples were grouped to form a "floating" calibration curve which was used to process only the samples among which the standards were distributed. This updating served to minimize any instrument instability. The calibration data fit a linear curve to within 1.6–5.5%, relative standard error of estimate, with a mean of 2.6%. These same data were later fitted to a least-squares quadratic curve with no improvement in fit.

Optical Emission Analysis. The spectrometer was a 2-m ARL Model 9500 Production Control quantometer equipped with a 990 lines/mm grating with 5.2 Å/mm reciprocal linear dispersion in the first order. The photomultipliers were either RCA or Hamamatsu 1P28, 931A, or equivalent and were distributed over three separate banks covering the spectral range of 2138–7700 Å. The ARL source unit was operated under the conditions specified in Table I to produce a high-voltage spark. A Spex 9010 Arc/Spark Stand fitted with a synchronous 20-rpm motor was used with Metbay rotrodes to excite the sample extract which was contained in a porcelain sample boat. The sample extract was 20% in nitric acid and contained 200 μg/ml indium and yttrium as internal standards and 2% lithium chloride as a spectroscopic buffer. The lead line at 220.4 nm, which was interference free, was used for the analysis line. The indium 451.1-nm and yttrium 324.2-nm lines were used for internal standards. The spectrometer readout system integrated the photomultiplier voltage signal for a fixed time after rotrode wetting and initial spark intervals. Both punched paper tape and typewriter records of the voltage signals for each channel were produced. All samples were analyzed twice. Spiked samples, replicates, blanks, and standards run as samples also were routinely analyzed with the samples.

The spectrometer paper tape output was batch processed on the PDP-8 minicomputer with special programs which corrected for background, determined least-squares calibration curves, corrected for interferences, subtracted blank corrections, updated both calibration curves and interferences, calculated both chemical and aerometric concentrations, and kept records of the parameters and analytical data involved in these procedures. Further details concerning the optical emission analysis procedure and data reduction will be published elsewhere (*9*).

Results and Discussion

Atomic Absorption Results. During a two-week period, all available 1970 NASN particulate samples collected on glass fiber filters were cut, extracted, and analyzed by atomic absorption. A total of 995 samples were analyzed including quality control samples. The results are listed in Table II. The mean quarterly composite level for all sampling sites was 1.1 μg/m^3 with a range of <0.1–6.7 μg/m^3. The 203 samples which were analyzed in duplicate showed analytical precision of 0.0–10.4%, RSD, with a pooled value (*10*) of 3.4%. An effective minimum detectable level of 0.50 μg/ml or 0.10 μg/m^3 was determined by choosing the most concentrated standard in any of the sets of nine standards that gave a difference be-

Table I. Emission Spectrometer and Excitation Conditions

Spectrometer	ARL 9500 quantometer, 2-m grating, 25-μ entrance and 75-μ exit slits
Grating	990 lines/mm, 5.2 Å/mm linear reciprocal dispersion in first order
Source unit	ARL E4700 high precision unit; electrode current, 4 rf amps; inductance, 50 μH; capacitance, 0.007 μF, two breaks/half cycle
Excitation stand	Spex 9010 Arc/Spark Stand with 20-rpm synchronous motor
Sample electrode	Metbay (ASTM D-1) rotrode, rotated at 20 rpm in plane of slit
Counter electrode	Metbay (ASTM C-5)
Sample boat	Coors #2 porcelain
Analytical gap	3 mm
Rotrode wetting time	30 s
Initial spark time	12 s
Integration time	36 s

tween the calculated and actual concentration greater than 50% relative deviation. Analysis of the blank filters gave an average lead content of 19 μg per 17.5 in.^{2} of composited sample, with a relative standard deviation of 57%. This blank value corresponded to 0.14 μg/ml in the analyzed solution and was below the effective detection limit of 0.50 μg/ml.

The range of recovery data from the spiked samples which were from 14 sites in nine different states was 80–108% with an average of 93% and a RSD of 9%. A *t*-test (*10*) showed no significant effect at the 98% confidence level. For the replicates (portions of the same filter extracted at different times) analyzed, the range of average lead levels was from 0.11 to 3.3 μg/m^3. The samples were from 14 different sites and states. The percentage difference between pairs relative to the mean ranged from 0.8 to 39% with an average of 9.8%. A pairwise *t*-test showed no difference between the samples and their replicates at the 95% confidence level. Similar tests of replicates from New York City showed 10% average RSD (*11*).

Optical Emission Results. The aliquots of the sample extracts for emission analysis were analyzed in duplicate over a six-week time period. Blanks, replicates, spikes, and standards run as blind samples were mixed with the samples. The results are summarized in Table II. The precision of reanalysis of the same solution obtained from the duplicate measurements was a pooled value of 11%, RSD. The blank value was well below the detection limit of 9.6 μg/ml or 0.15 μg/m^3. The standards as samples recovery of 100% (6% RSD) showed that the spectrometer-data processing system was operating with high accuracy with regard to standards analysis.

Samples chosen for spiking were selected to represent a variety of sites and particulates. The range of recovery data from the spikes was 79–108% with an average of 102% and a RSD of 8%. A *t*-test showed no significant effect at the 90% confidence level. The replicates gave a difference between pairs of 0.3–44% with an average of 15%. A pairwise *t*-test showed no significant difference at the 90% confidence level between samples and their replicates.

Table II. Comparison of Atomic Absorption and Optical Emission Lead Analyses of 1970 NASN Samples

	AA, 283.3 nm			OES, 220.4 nm		
	N	Concn, μg/ml	Value	*N*	Concn, μg/ml	Value
Precision, RSD, %[a]	203	7–20	3.4	800	9.6–360	11
Replication, av diff, %[b]	14	0.5–16	9.8	23	22–210	15
Standards as samples recovery, %[d]				25	24–240	100[c] (6.1%)
Spike recovery, %	14	1.7–22	93 (9%)[e]	15	13–220	102[c] (8%)
Blank value, μg/in.^{2} [f]	14		1.1 (57%)			[g]
Detection limit, μg/ml			0.50			9.6
μg/m^3 [h]			0.10			0.15
Analysis time, man-hour/sample[i]			1.2			1.4

[a] Repeat analysis of the same solution. *N* solutions were analyzed in duplicate. [b] Difference between sample and replicate expressed as a percentage of the mean. [c] Weighted average. $\bar{X}_w = [\sum(\bar{X}_i N_i/S_i^2)]/\sum N_i/S_i^2]$ where N_i is the number of data in the *i*th set with average $\bar{X}_i$ and standard deviation S_i. [d] Standards run as blind samples. [e] Data in parentheses are precision data, expressed as % RSD, for value cited. [f] Expressed as μg Pb per in.^{2} of blank filter. [g] Below detectable. [h] Based on an average air volume of 2500 m^3. The AA solution is diluted by 1:12.5 relative to the OES solution. [i] Includes all steps from cutting filters through data reporting.

Comparison of Methods. The only difference between the performance data obtained by the two methods was the precision of reanalysis and detection limits. All other parameters agreed within their precision limits. The precision of reanalysis was 3.4%, RSD, by atomic absorption and 11% by optical emission. The higher detection limit by emission analysis was partially compensated for by the dilution necessary for the atomic absorption analysis, and the aerometric limits were very close, i.e., 0.10 vs. 0.15 μg/m^3. The analysis times per sample including all steps from cutting the filters through data reporting were very similar—1.2 man-hours for atomic absorption vs. 1.4 man-hours for optical emission. Of course, the emission analysis also produced 23 other elemental analyses per sample in this time period.

The 1970 NASN samples were divided, following extraction, into two aliquots, one being used for the analysis for lead by atomic absorption and the other reserved for multielement analysis by optical emission spectrometry. It was therefore possible to compare the results obtained on the same extract solutions by two entirely different analytical techniques. Some 203 of the 945 atomic absorption data were averages of two determinations, while all of the optical emission data were determined in duplicate.

Considering only data above the detection limit of either method reduced to 795 the number of data sets available for comparison. The detection limit was 9.6 μg/ml (0.15 μg/m^3 for 2500 m^3) for optical emission and 0.50 μg/ml (0.10 μg/m^3 for 2500 m^3) for atomic absorption. For all 795 samples, the average difference between the two methods relative to the mean was 14% with a range of 0–87%. This average agreed with the combined RSD's of the two methods of 14%. If the comparison was restricted to the more reliable duplicate atomic absorption data for 203 samples, the average difference was 9.6% with a range of 0–52%. A paired *t*-test of the 203 data sets showed a significant difference between the two methods at the 99% confidence level. A frequency distribution of the 795 differences between the two methods showed that the mode (most frequent value) was 8% difference with the optical emission data being larger. A reported comparison of atomic absorption and dc arc emission data for one particulate matter sample collected in Osaka gave a 17% difference (*12*).

Atomic Absorption Interferences. Our spike recovery data of 93% with 9% RSD do not support the large interferences found by Burnham et al. (*3*) on the 283.3-nm line with their Illinois samples. The agreement of our atomic absorption and optical emission data (obtained with the 220.4-nm line) in general and the spike recovery data in particular proves that no significant atomic absorption interferences occurred with these samples from widely distributed sites across the United States. The small interference reported by Zdrojewski et al. (*7*) cannot be detected within the precision of our data.

Conclusions

The results of this study showed that the standard addition method for analyzing particulate lead is not required with the 283.3-nm line using the present procedure. Both the optical emission and atomic absorption data showed that the standard NASN extraction and analysis procedure gave excellent (98% average) spike recoveries for lead on a wide variety of particulate samples. No significant difference between lead content of different sections of the same filters was found by either method at the 95% confidence level. The lead content of glass fiber filters extracted with the NASN procedure was approximately 1 μg/in.^{2}. The very good agreement of the analysis results by both methods for 800 widely different particulate samples collected by the NASN supports the use of atomic absorption analysis for precise special studies and optical emission analysis for rapid routine survey studies.

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Decomposition of Solid Organic Materials in the Deep Sea

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■ Samples of solid organic materials (various seaweeds and woods, paper, chitin, fish meat, foodstuffs), incubated for up to 15 months in the deep sea at depths of 1830–5300 m, degraded at markedly reduced rates as compared to those of controls incubated in shallow water or in the laboratory at equal temperatures. Similar results were obtained in more refined experiments with solidified agar, starch, and gelatin placed at defined positions above, below, and at the sediment surface by the research submersible *ALVIN*. Removal of these materials by invertebrate feeding appeared to exceed the rate of degradation by microorganisms at the northern station (continental slope off Nantucket), but not at the southern station (Tongue of the Ocean, Bahamas). In connection with other results, it appears that a population of free-living (nonintestinal) microorganisms specifically adapted to deep-sea conditions does not exist.

In recent years, an advancing deep-sea technology, combined with growing interest in the ocean as a recipient of waste materials, prompted studies on the fate of extraneous organic materials in deep waters and sediments. In the present paper, we are reporting observations collected over the last five years on the degradation of a variety of solid organic materials submerged in the sea or deposited on the ocean floor at depths of up to 5300 m for time periods of 5 weeks to 15 months. Our interest in this area was originated by findings following the *ALVIN* accident (*1*) and resulted in quantitative studies on rates of microbial decomposition of dissolved organic substrates (*2*). These measurements required closed systems (sample bottles) and well-mixed soluble materials which were inoculated and incubated on the deep-sea floor with the aid of the rebuilt research submersible *ALVIN*. These in vitro determinations are quantitative but have the disadvantage of excluding direct and permanent contact with the surrounding water and the possible activity of the deep-sea benthic fauna other than microorganisms.

On the other hand, observations on the decomposition of solid organic materials under truly natural conditions (in an open system) include the effects of leaching, dilution, and mechanical breakdown and can never result in quantitative and reasonably reproducible figures. Data on the degradation of substrates of complex composition such as wood, seaweeds, animal carcasses, trash components, and food materials can at best be semiquantitative, based on various means and arbitrary units of observation. In spite of these inherent limitations, such studies are of practical value and represent a necessary and important complement to our quantitative and exclusively microbiological rate measurements.

In this paper we report results of various types of deep-sea incubation of solid organic materials: samples enclosed in bottles initially filled with inshore surface water, samples enclosed in empty bottles which fill with seawater on descent at ca. 200 m depth, samples enclosed in empty bottles which fill at the deep-sea floor, samples contained in plastic bottles with large holes, samples (of rigid materials) attached to racks, and samples (of semisolid materials) enclosed in plastic tubes with openings and inserted into the sediment.

Materials

The organic materials to be exposed in situ to deep-sea conditions were chosen with regard to natural occurrence and complexity on the one side and experimental reproducibility on the other. They were primarily carbohydrates or proteins. Cellulose and chitin are materials which may be part of the "refractory" particulate matter sedimenting to deep water and in part reaching the sea floor prior to complete decomposition. Cellophane and various kinds of paper have generally been used for the demonstration of aerobic and anaerobic cellulose decomposition.

Different results were expected from complex fresh plant material since they offer a variety of supplementary nutrients to microorganisms or may serve as food for macroorganisms which would not assist in the decomposition of purified cellulose alone. Fresh plant material of marine origin, sea lettuce (*Ulva lactuca*), rock weed (*Fucus*), and suspensions of unicellular diatoms were used along with terrestrial vegetal matter such as leaves of deciduous trees (maple), and of plants (Philodendron). Wood samples (pine, beech, and balsa) belonged to the same category. Rice grains, boiled and unboiled, and white bread were complex starch sources, the former commonly used as "bait" for certain aquatic microorganisms. For comparison, purified starch in solidified form was also used. Agar represented a sulfonated polysaccharide commercially produced from marine algae and utilized as a substrate by agarolytic bacteria which are common in seawater (*3*). Cleaned sections of lobster tails and crab claws were used as a source of chitin. Fresh fish meat and purified gelatin served as proteinaceous materials.

Procedures

Sample Packages. Packages containing a variety of materials were attached to the cables of oceanographic buoys moored on a transect between Woods Hole, Mass., and Bermuda. These experiments, conducted at a depth of 5300 m, were complemented by identical sets of materials exposed to coastal waters at a depth of 38 m. The plastic packages (Figure 1) had numerous holes of 25 mm diameter to allow free passage of seawater to the inside. The test materials were held in plastic bottles with holes of 13 mm diameter (seaweeds, etc.) or mounted on racks (wood samples, etc.) dependent on its rigidity. In addition, materials were also kept in closed bottles (120 ml) inoculated with Eel Pond water. This procedure is based on the assumption that most solid organic materials sinking to the sea floor are heavily contaminated with surface-originated microorganisms. In other bottles, initially containing no water, the pressure equilibrating serum caps were punctured to allow filling by pressure during descent. Tests in pressure chambers have shown that the filling took place largely at a depth of 200–250 m with only small amounts of water entering during further descent (*1*). The boxes were attached to a cable moored at 5300 m depth, ca. 10 m above the sea floor in the Atlantic Ocean (34°02′N, 69°59′W) for 7 months.

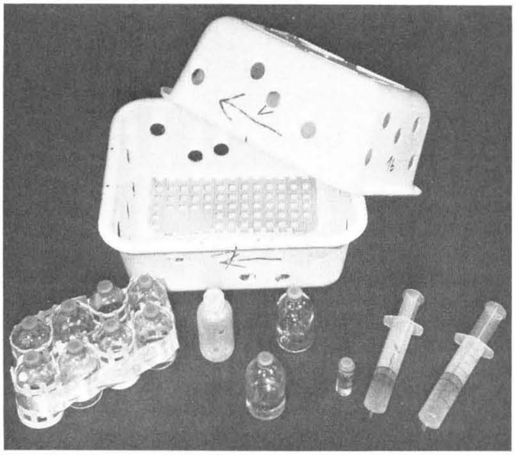

Figure 1. *Sample Packages* containing various types of bottles, vials, syringes, etc., for in situ incubation of solid and dissolved organic materials on deep-sea moorings at 5300 m depth

As controls, parallel samples were held at approximate in situ temperature (3 °C) and at normal pressure. They were examined periodically during the test period. Observations on signs of degradation and simultaneous growth of microorganisms were done on a visual scale only. If possible, dry weight measurements were conducted.

Bottle Racks for In Situ Inoculation. Although all sample containers described above allowed for contact, i.e., inoculation with water from the sea surface, a bottle rack was constructed that provided for inoculation of samples exclusively from near bottom waters or sediment slurry. Bottles with punctured serum caps, as described above, were housed in pressure-tight aluminum cylinders (Figures 2a and 2b), which were flushed with N_2 gas and then evacuated. A valve operated by the mechanical arm of the research submarine *ALVIN* allowed flooding of the cylinder after transport to the sea floor, thereby inoculating the sample bottles. This device has been successfully used in quantitative studies on microbial transformations of dissolved organic substrates (*2*). At the same time, this approach has been applied to investigate the exclusive activity of the deep-sea microflora on presterilized solid organic materials (such as seaweed and various types of wood and paper), i.e., in the absence of surface-originated microorganisms carried down to the incubation site. This type of experiment is necessary to prove or disprove the existence of a distinct deep-sea microflora.

Sediment Racks. To supplement the quantitative data on in situ inoculation and incubation of agar, starch, and gelatin obtained in closed systems (*2*), semiquantitative measurements were obtained in open systems. For this purpose, Plexiglas racks containing 20 polycarbonate tubes were constructed (Figure 3). Each tube was sectioned in four compartments (E) of equal size (about 1 ml) by silicone plugs (G). Each compartment was opened to the outside by a hole of 4 mm in diameter (F). When mounted on the rack (A, B) and deployed, the tubes were partly inserted into the sediment (H). The sections remaining above the sediment surface were shielded by a Plexiglas cage with 13-mm holes (C) to allow free flow of seawater but prevent access of larger animals.

Prior to the deployment of these racks, the compartments of the tubes were filled with the sterilized substrates (agar 1.5%, starch 12%, and gelatin 12% in 1% agar) and kept refrigerated after solidification of the media. There were 6 tubes (24 samples) for each substrate. One-half of these samples were supplemented with nutrients: 0.2% NH_4Cl and 0.05% KH_2PO_4. Special tubes were not compartmentalized but filled with single pieces of wooden pine pegs.

The racks to be placed in the deep sea were transported to the bottom at 1830 and 1960 m by the research submarine *ALVIN* for incubation periods of 12 and 15 months, respectively. With the mechanical arm the rack was pushed into the sediment to the depth set by horizontal wings fastened to the Plexiglas cage (Figure 3D). The openings of each of the tubes were then positioned as follows: top hole 3.5 cm above sediment surface, next lower hole at the water/sediment interface, next lower hole 3.5 cm, and bottom hole 7.0 cm into the sediment. Following retrieval of the racks from the deep sea, the tubes were removed and examined for loss of contents, liquefication, cracking of gel, colonization, and invasion by meiofauna and were finally analyzed for percent of remaining substrate. Agar and starch were tested for anthrone positive material and gelatin by the Lowry method based on sterile control media. For comparative observation, one rack was submerged in a similar fashion into the Eel Pond at a depth of 2 m and retrieved after 5 weeks.

Analytical Determinations. In some cases, specified in the following section, a number of simple analytical determinations could be applied. Dry weight measurements were made whenever aliquots of a particular sample and the appropriate controls were available. Wood, paper, and seaweed samples were dried in an oven at 103 °C to constant weight after washing to remove salts. If the determinations could not be conducted immediately after retrieval, the microbial activity was stopped by injecting 1.0 ml of 0.2% $HgCl_2$ into the bottles containing the samples. Starch and agar were determined by the anthrone method following the procedure described by Viles and Silverman (*4*). Gelatin was determined as protein by the method of Lowry et al. (*5*).

Results

The observations and data reported below refer to the following "sample packages", "sediment racks", and one "bottle rack".

Package #1 (position: 34°02′N, 69°59′W, approximately 450 miles south of Woods Hole) was set on October 9, 1970, at a depth of 5300 m (approx. temperature 2 °C) and was retrieved on May 4, 1971 (time of incubation: 7 months). As a control experiment carried out in shallow water, *Package #2* (position:

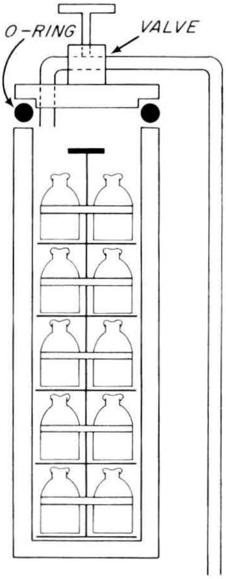

Figure 2a. Pressure housing for sample bottles to be lowered by research submersible *ALVIN* and opened for in situ inoculation and incubation of samples in the deep sea

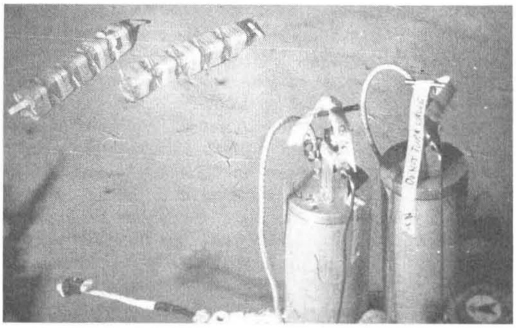

Figure 2b. Two deposited *Bottle Racks* and two pressure housings in foreground (permanent station at 39°46′N, 70°41′W at 1830 m depth)

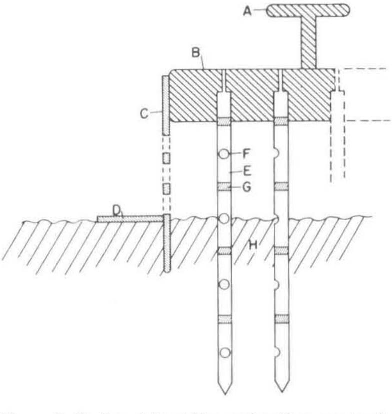

Figure 3. *Sediment Rack* (for explanation, see text)

41°17′N, 71°01′W, 19 miles southwest of Woods Hole) was deployed on March 10, 1971, at a depth of 38 m (temperature range 1–12 °C) and was retrieved on August 16, 1971 (time of incubation: 5 months).

Sediment Rack #1 (position: 39°46′N, 70°41′W, northern permanent deep-sea station, approximately 120 miles south of Woods Hole) was set on June 22, 1971, at a depth of 1830 m (approx. temperature 3 °C) and was retrieved on June 12, 1972 (time of incubation: 12 months). Used as a control, *Sediment Rack #2* was set on September 19, 1972, at a depth of 2 m in the Eel Pond, Woods Hole (approx. temperature range 13–20 °C) and was retrieved on October 25, 1972 (time of incubation: 5 weeks). *Sediment Rack #3* (position: 24°53′45″N, 77°39′30″W, southern permanent station, approximately 5 miles southwest of New Providence Island in the Tongue of the Ocean) was set on January 20, 1974, at a depth of 1960 m (approx. temperature 7 °C) and was retrieved on April 19, 1975 (time of incubation: 15 months).

A *Bottle Rack* for in situ inoculation and incubation of 20 bottles was set and retrieved at the same site and on the same dates as the *Sediment Rack #1*.

Sample Packages. Thalli of *Ulva* incubated in Eel Pond water and closed bottles stayed intact in all samples. The water became faintly turbid in the bottles suspended in Package #2 and in the controls, and high populations of bacteria attached to the plant material were observed microscopically. The decrease in dry weight of *Ulva* was 8% in Package #1 and 19% in Package #2. The losses in the refrigerated controls (constant 3 °C) were 19 and 12%, respectively.

In parallel bottles containing freshly harvested *Fucus*, the plant material in Package #1 and Package #2 looked intact but had lost rigidity in the latter and broke apart on touch. Microscopy revealed large populations of microbial cells attached to the plant surface. The decrease in dry weight of *Fucus* was 3.5% in Package #1, 11.3% in Package #2, and 5% and 3%, respectively, in the refrigerated controls. One bottle in Package #2, as well as the corresponding control, had become anaerobic. Relatively high temperatures (up to 12 °C) occurring during incubation of Package #2 may be the reason for the comparatively high microbial activities in contrast to those observed in the controls kept at constant 3 °C.

Suspensions of washed cells of *diatoms* in Eel Pond water (5.4 mg dry weight/bottle) showed a loss of 7.5% in Package #1 as compared to 13% in the control This material was not included in Package #2.

Boiled and unboiled *rice*, as a uniform source of vegetal carbohydrate, likewise incubated in Eel Pond water containing high numbers of microorganisms, produced abundant bacterial and fungal growth (turbidity) in Package #2 as well as the controls. The water in the bottles containing rice in Package #1 did not show any turbidity. The *rice* grains stayed intact in all samples, however. It is possible that nitrogen limitation prevented complete breakdown in Package #2 and the controls. No degradation and only a slight turbidity were found in all samples containing white bread, and we believe that preservatives (propionate and benzoate) normally added to this type of bread may account for this result.

In addition to closed bottle experiments, the degradation of *fish meat* as a source of protein was also studied in bottles contained in Package #1 which self-inoculated at a depth of about 200 m. The results are shown in Figure 4. All three bottles contained an equal amount of *fresh meat* of bass. Of the two bottles at right, filled with Eel Pond water, the control (far right) showed disappearance of all solid material and the production of a heavy suspension of putrifying bacteria when incubated at 3 °C for 3 weeks. The bottle in the center was incubated in Package #1 and showed slight turbidity only, the appearance and rigidity of the *fish meat* having hardly been affected. Virtually the same was found in the self-inoculated bottle at left which was also incubated with Package #1. The degree of decomposition was obviously not affected by the two vastly different microbial inocula. Water was displaced from the bottle at left by the liberation of dissolved gas (air) during and after retrieval. Gas bubbles caused the piece of meat to float up. Since microbial growth appeared to be quite similar in the two bottles to the left, inhibition by the amount of oxygen dissolved during filling of the bottle at 200 m depth seems to be unlikely.

Pieces of *tuna meat* incubated in Eel Pond water and submerged with Package #2 degraded entirely. This complete decomposition (disappearance of solid material) could certainly have occurred before the end of the 5-month incubation period. The control held at 3 °C was similarly degraded after 60 days. All these bottles had turned anaerobic. One bottle in Package #2 containing unsterile tuna meat in sterile seawater showed heavy turbidity, but chunks of meat were still visible and the water was still aerobic.

Sample bottles with sizable holes (18 mm diameter) were used as "open systems" to expose some suitable materials to the environmental conditions thereby sacrificing, however, all means of quantitative or semiquantitative assessment of degradation. With materials that were incubated in the deep sea in open systems, parts of the softened or half degraded matter could be lost from the punctured bottles by the flow of water during retrieval (washing action).

The degree of degradation of white *paper towels* and *bond paper* was quite similar in the Packages #1 and #2. The material was softened, discolored, and fragile, more so the *bond paper* than the *paper towels*. The paper samples in Package #2 were slimy and gave off an odor of sulfide in cases where sediment had settled in the folds of the paper. In contrast to the observations on other materials, the degree of degradation in the controls (*paper* suspended in Eel Pond water and kept at 3 °C) was much less than had occurred in situ. The immediate exposure to an active bottom flora of cellulose degrading microorganisms may be the explanation. In the only case where strips of cellophane were tested, the degradation in Package #1 exceeded that observed in Package #2 and may possibly be explained by mechanical removal during recovery as mentioned above.

Fresh *green leaves* of maple and *Philodendron* remained visibly undegraded in both packages as well as in the controls. Differences in discoloration were slight and insignificant. An exception was one case where *Philodendron* leaves in Package #2 exhibited some deterioration of the cellular structure on several leaf tips.

Chitin, on the other hand, has almost entirely disappeared in both packages. The remaining pieces were soft and broke apart when removed from the racks. There was no clear distinction in the degree of degradation in Packages #1 and #2.

Wood samples (beech and balsa) remained macroscopically and microscopically intact when submerged in closed bottles (filled with Eel Pond water) in Packages #1 and #2. When openly exposed to the environment, however, the samples of both packages showed a whitish surface layer and microscopic signs of microbial attack. No feeding marks of animals (borers) were observed in these experiments.

Bottle Racks. Although primarily used for quantitative degradation studies of dissolved organic substrates, deep-sea inoculations were also conducted for solid materials such as paper, wood, and seaweed. Dry weight losses were minute at the end of the 1-year incubation period at 1830 m (Table I). The wood showed less visible changes (no whitish surface layers) than those samples exposed openly on racks. In both cases, the results were different from Turner's (*6*) observations indicating that wood panels planted into the sediment were invaded by boring bivalves. This was true, however, when wood dowels were used in connection with the sediment racks as reported below.

Sediment Racks. In Sediment Rack #1 (depth 1830 m, incubation time 12 months), no major liquefication of *agar* was found after the 1-year incubation period. In most tubes and in all four sections, the contents appeared almost unchanged. In contrast, the results of the anthrone analysis (Table II, A) indicate a substantial percentage of loss of anthrone-positive material. This may well be due, however, to leaching of the highly soluble sulfated galactans which represent about 40–50% of the Difco agar used (*3*).

The supplementation with ammonia and phosphate had no detectable effect on the rate of agar degradation. Therefore, in Table II average rates for all five tubes are given. The sixth tube was transferred to a vessel with sterile seawater immediately after retrieval and incubated for another 4 months at 15 °C before analysis. These data are included in Table II, B.

As a direct sign of degradation, there were small depressions, 1–3 mm in depth, around the exposed surfaces in several cases. The microscopic examination of some white spots observed on these surfaces revealed large populations of microorganisms primarily consisting of vibrio- and rod-shaped bacteria.

Relatively little liquefication of *agar* had also occurred in the tubes incubated in the Eel Pond (Sediment Rack #2) for a five-week period. There was a considerable visible loss of material in the section exposed at the sediment-water interface leaving behind highly turbid but still solidified *agar* with a distinct odor of sulfide. As reflected in Table II, C, this section showed a particularly high degradation of the substrate. Although, as mentioned above, the supplementation with inorganic nitrogen and phosphate sources had no effect, the addition of gelatin (12 mg/ml) increased the rate of agar degradation considerably. Polychaetes had entered the two upper sections of the gelatin-supplemented agar tubes. All

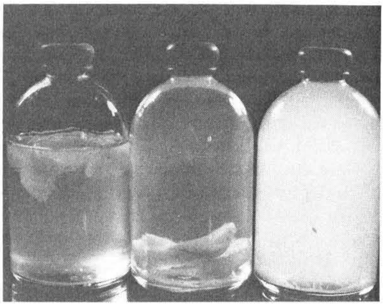

Figure 4. Samples of fish meat incubated at 5300 m depth for 7 months (left and center) and in laboratory for 3 weeks at equal temperature (right)

Table I. Substrate Lost and Percent of Initial Dry Weight Remaining After One Year of In Situ Incubation at 1830 m

	Substrate lost, mg	% Remaining
Bond paper	1.8	99.4
(Duplicate)	5.0	98.4
Paper towel	1.5	99.0
(Duplicate)	0	100.0
Balsa wood	0	105.0
Birch wood	0	102.0
Ulva thalli	2.0	98.9

Table II. Remaining Quantities of Agar and Starch (as Determined by Anthrone Technique) and Gelatin (as Determined by Lowry Technique)[a]

Initial amt of substrate, mg/ml	1	2	3	4
A Agar (15)	7.25 (48%)	8.72 (58%)	7.78 (52%)	8.16 (54%)
Starch (120)	88.0 (73%)	88.5 (74%)	87.2 (73%)	85.6 (71%)
B Agar (15)	3.9 (26%)	7.9 (52%)	8.4 (56%)	8.9 (59%)
Starch (120)	44.0 (36%)	59.0 (49%)	39.0 (33%)	51.0 (43%)
C Agar (15)	11.6 (77%)	5.6 (37%)	10.6 (71%)	9.3 (62%)
Starch (120)	66.0 (55%)	50.0 (41%)	74.0 (61%)	70.0 (58%)
Agar (15)	7.0 (46%)	8.2 (54%)	9.1 (60%)	6.7 (44%)
+ Gelatin[b]				
D Agar (15)	7.80 (52%)	5.9 (39%)	11.7 (78%)	11.5 (77%)
Starch (120)	17.1 (14%)	23.6 (20%)	56.8 (47%)	80.0 (67%)
Agar (10)	1.69 (17%)	2.9 (29%)	8.2 (82%)	8.5 (85%)
+ Gelatin (120)	16.0 (13%)	12.0 (10%)	18.1 (15%)	32.7 (27%)

[a] Initial amount incubated (A) for 12 months at 1830 m (Sediment Rack #1), (B) same, but with an additional 4-month incubation in the laboratory at 15 °C, (C) for 1 month in shallow inshore water (Eel Pond) (Sediment Rack #2), and (D) for 15 months at 1960 m (Sediment Rack #3). Numbers 1–4 refer to the location of the tube openings: (1) 3.5 cm above sediment surface, (2) directly at the sediment surface, (3) 3.5 cm and (4) 7.0 cm below the sediment surface. [b] Gelatin (initial amount 12 mg/ml) not determined.

four sections were highly turbid, partly blackened, and showed gas bubbles within the agar. Considering the different incubation times, the average degradation rate in these tubes incubated in Eel Pond can be estimated to be about nine times faster than in the deep-sea tubes.

In Sediment Rack #3 (depth 1960 m, incubation time 15 months) the visible degradation of *agar* showed a different picture when compared to the tubes of Sediment Rack #1. From the two upper sections of the tubes, exposed to water above the sediment and to the sediment surface, the *agar* appeared to be removed about 50%, but there was no sign of animal feeding. The remaining material was clear and unchanged in appearance. In all six tubes, the *agar* in the third section (3.5 cm below the sediment surface) exhibited a black zone at the opening which extended as a plate through the otherwise clear material. An odor of sulfide was detected in these sections. Above this zone, a thin layer of whitish matter was found microscopically to consist of a heavy population of motile rods and two types of filamentous cells. One of the latter resembled *Beggiatoa* containing sulfur granules within filaments of ca. 12 μ in diameter, the other an *Actinomyces*-type organism with filaments of ca. 2 μ in diameter. The bottom section of the tubes (7 cm below the sediment surface) exhibited no visible loss of *agar* and no black or whitish discoloration. Quantitative measurements of the *agar* remaining appears in Table II, D, whereby the leaching problem has to be considered. The nutrient-enriched samples did not show an enhancement of *agar* decomposition.

The *starch*-filled tubes in Sediment Rack #1 also showed little visible signs of degradation. The white material did not change in appearance, and there was a little loss around the openings of the two upper sections only (Figure 5). In a few occurrences of slight blackening in the sections exposed at the sediment-water interface, a variety of bacteria could be isolated including a spirochaete. In three tubes the sections at the sediment surface were invaded by polychaetes.

The starch decomposition in the parallel samples incubated in Sediment Rack #2 (Eel Pond) was again surprisingly low, whereby the relative short time period must be considered. Most extensive degradation, as well as black layers around the openings, and smell or hydrogen sulfide occurred in all sections exposed to the sediment-water interface.

In Sediment Rack #3, an estimated 50–60% loss of *starch* occurred in the two upper sections while the remaining material appeared visibly unchanged. Little or no loss was apparent in the two lower sections exposed in the sediment. A greater loss than visibly estimated was shown for all sections by chemical analysis (Table II, D). There was no indication of sulfide production in any of the tubes. Nutrient enrichment had no effect on *starch* degradation in any of the sediment racks.

Tubes filled with 12% *gelatin* posed problems of melting due to high temperatures during handling. In Sediment Rack #1 some of the material was lost during deployment. For this reason, no quantitative assessment was made after recovery. To overcome this problem, the 12% *gelatin* was added to a 1% *agar* base in Sediment Rack #3. Although the visible removal of this material in the upper two sections was extensive (approx. 80%), there was no blackening, turbidity, or traces of animal feeding. In the presence of *gelatin* the degradation of *agar* in the upper two sections was enhanced (Table II, D), while again the supplementation with NH_4Cl and KH_2PO_4 showed no effect.

Sediment Racks #1 and #3 also contained pine wood dowels inserted into the tubes without compartmentalization. At the northern station, wood boring bivalves had entered and largely consumed the dowels down to the level of the water/sediment interface but not below. The borers were retrieved and identified by R. Turner who found the same species in wood panels planted into the sediment at the same station. No borers invaded the wood-filled tubes of Sediment Rack #3 at the southern station.

Discussion

The general finding of decreased degradation rates of solid organic materials in the deep sea, as based on shallow water and laboratory controls, varied with respect to the site of incubation and the type of substrate used, but especially with respect to the mode of exposure to the environment. It appeared to be of major significance whether or not organisms of certain size ranges had access to the test materials. Inoculation of the samples through an opening slit of less than 1 mm resulted in restricted degradation activity of dissolved as well as solid materials during subsequent in situ incubation. If, on the other hand, larger areas of direct contact between sample and environment were provided (at the same time restricting the experiments to solid and semisolid materials and foregoing truly quantitative measurements), animals had access and increased the apparent rate of degradation significantly. Sieburth and Dietz (7) found similar contrast between states of preservation of foodstuffs encased or not encased during incubation in the deep sea. Presently, we are incubating a variety of solid organic materials under somewhat more sophisticated conditions of controlled access (openings of 0.09–100 mm^2) deployed by the research submersible. In comparing these studies to microbiological measurements, it

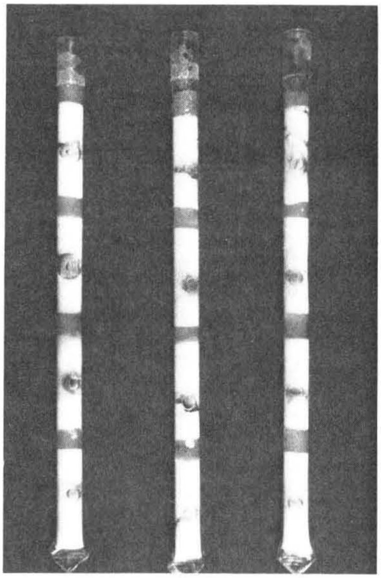

Figure 5. Compartmentalized tubes from *Sediment Rack* filled with starch and incubated at 1830 m depth for 12 months

must be considered, however, that mere removal of a substrate by feeding animals is not, a priori, equivalent to degradation in the biochemical sense.

As in the earlier work by Muraoka (*8, 9*), we have also recorded animal attack on wood samples and, in addition, on solidified agar and starch. Turner's (*6*) findings at the northern station in 1830 m of water have been mentioned above. Indirect indications of rapid animal activity in deep waters concerned a photographic recording of a diverse epibenthic fauna locating and consuming bait at a depth of 2000 m (*10, 11*). Dayton and Hessler (*12*) discussed these observations with respect to food limitations of these populations. Quantitative measurements have shown that in situ respiration rates of fish at a depth of 1230 m (*13*) are about two orders of magnitude slower than those observed in shallow water specimens. Yet, the agility in locating the planted food sources and the rapid consumption by epibenthic invertebrates and fish appears, at the present state of this research, to be in contrast with the recorded inhibitory effects of hydrostatic pressure on microbial activity. However, compatible biochemical measurements have not yet been done. It has been hypothesized (*2*) that the major site of microbial activity in the deep sea may be confined to the intestinal tracts of benthic animals where the enriched nutrient milieu will enable the microorganisms to decompose refractory materials in an endosymbiontic fashion. Studies in this direction are underway.

Organic matter reaching the deep ocean floor under natural conditions represents materials degraded slowly because of its refractory nature (cellulose and chitin and other polymeric material of planktonic origin partly contained in fecal pellets), and materials with rapid sinking rates such as fish carcasses. Scavenging deep-sea animals may largely depend on the latter. Our data indicate that this fauna may benefit from a lesser competition by the free-living microbial population as compared to comparative conditions in surface waters and sediments.

Most striking were the observations on the relatively slow decomposition of fish meat (Figure 4) in closed bottles incubated in deep water. Approaches to make practical use of this phenomenon involved testing the degree of preservation of freshly caught fish packed in plastic and submerged into deep water (*14*). The slow rate of initial enzymatic conversions, however, turned out to be sufficient to affect fish meat quality and taste to an intolerable degree. Nevertheless, in laboratory experiments at refrigerator temperature, fish could be stored 2–3 times longer at 270 atm than at normal pressure (*15*).

The data and observations on the degradation of solid organic materials show much less reproducibility than those obtained from dissolved substrates. The most obvious reason is that the invertebrates are less homogeneously distributed than microorganisms and that the latter are present in much higher numbers. In addition to the microorganisms' ability for long survival in dormant stages, they revive quickly if brought into contact with a food source as shown on streak plates.

The little difference between degradation rates recorded with microbial populations from inshore surface waters and those from the deep sea, both incubated in the deep sea, appears to indicate the absence of a free-living microbial flora specially adapted to deep-sea conditions. No case of a "barophilic" response was observed, i.e., an increase of activity at elevated pressure as compared to the 1 atm control at equal temperature. There is no final proof of this fact, of course. An observation reported recently may indicate the existence of such barophilic responses. Seki et al. (*16*) lowered two rubber bulbs (J.-Z. sampler, 17) containing a peptone-yeast extract medium to 5200 m for in situ inoculation and a 5-day incubation. The population collected in one of the bulbs showed faster growth, in the other one equal growth, as compared to a 1 atm control. Unfortunately, no culture was kept. There is also some doubt (*17*), and the lack of direct evidence, that the rubber bulbs do open and fill in the presence of high pressure.

To arrive at more substantial proof of barophilic or nonbarophilic behavior, it is necessary to eliminate the inherent restriction of in situ incubation studies to mere end-point measurements and to design a procedure that allows multiple withdrawals of subsamples from individual populations for successive activity measurements. To make this possible, without sacrificing the incubation under unchanged natural conditions, well-insulated pressure-retaining sampler and incubation vessels have been developed (*18*). Growth and activity measurements on populations retrieved from 1800 to 3000 m with this new tool (*19*) in principle confirm the absence of a pressure-adapted microbial population.

It is interesting to note that the addition of nutrients (ammonia and phosphate) to the samples of agar and starch in the sediment racks had no apparent effect on the rate of degradation. Explanations may be: quick leaching of the soluble N- and P-sources, and their natural availability in sufficient concentration, corresponding to the low rate of growth limited by a factor other than lack of nutrients. The contrast between the unchanged appearance of agar after the 1-year incubation and the anthrone data has been explained by the leaching of anthrone-positive materials (*3*). The additional incubation of agar and starch tubes for another 4 months in the laboratory at 15 °C after removal from the deep sea resulted in a general increase of the degradation rate (Table II, B). Here, the two lower sections of the agar tubes pose an obvious exception, indicating possibly a limited leaching of soluble agar constituents in the small closed system. Such variable results show the inherent drawback of semiquantitative approaches which are, however, inevitable in the study of in situ degradation under natural conditions.

As a general observation, visible degradation of agar, starch, and gelatin was strikingly less in the tube sections buried in the sediment as compared to the two upper sections. This applied to microbial as well as animal (feeding) activity and has also been observed by Muraoka (*8, 9*). The chemical analysis reflected this effect only for the samples incubated at the Tongue of the Ocean (Table II, D).

One obvious question arising from these results regards the fate of man-made solid organic waste materials dumped into the deep sea. Microbial mineralization (the recycling of nutrients) will occur at a retarded rate (one to two orders of magnitude) than in shallow waters or even much slower than that in land-fill operations. Oxygen depletion can be expected to occur depending on the type of containment and on the local current pattern. The effect on the benthic and epibenthic fauna is difficult to predict from our present knowledge. Most of the waste material may not serve as suitable food, and consumption by animals may ultimately depend on the activity of microorganisms as primary degraders.

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Kinetic Studies of Sulfur Dioxide Absorption by Manganese Dioxide

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■ Absorption of sulfur dioxide from SO_2–N_2 mixtures by manganese dioxide was studied at temperatures from 573 to 723 K, with SO_2 concentrations from 0.2 to 1 vol % and pellets of manganese dioxide $\frac{5}{16}$ in. (7.94 mm), $\frac{3}{8}$ in. (9.52 mm), and $\frac{7}{16}$ in. (11.11 mm) in diameter. The absorption rate, the total pore volume, and the specific surface area of a reacted pellet all decreased with fractional conversion of oxide to sulfate. The maximum conversion observed was always less than 60%. Microscopic examinations of reacted pellets indicated that reaction was nontopochemical at the temperatures studied. A model was proposed to describe the reaction kinetics, assuming the manganese dioxide pellet to consist of porous particles whose size remains unchanged during reaction. Equations were derived to relate the particle porosity and the specific surface area of a reacted pellet to conversion. The reaction was assumed to be irreversible and first order with respect to SO_2 concentration and also proportional to the reacting surface area. The agreement between the model and experimental data was satisfactory. An activation energy of 10.3 ± 0.8 kcal/g mol ($4.3 \pm 0.3 \times 10^7$ J/kg mol) was obtained.

Manganese oxides react readily with sulfur dioxide in a flue gas environment to form manganese sulfate (*1*). Regeneration of oxides from the sulfate can be accomplished by indirect electrolysis (*2*), oxidation in ammonia solution (*3*), or thermal decomposition (*4*). Commercial application of the manganese oxide process is under serious consideration in Japan after successful tests on the pilot and semicommercial plant scale (*3*). However, very little on the kinetics of sulfur dioxide absorption by manganese oxides has been published.

Lacey et al. (*5*) reported a study of the absorption of SO_2 by γ-Mn_2O_3. Their rate data seem to indicate that the absorption is controlled by both diffusion and chemical reaction. A homogeneous model with the reaction assumed to be first order with respect to both the gas and the solid was proposed, and a numerical technique to solve the unsteady-state diffusion equation for a semi-infinite solid was illustrated.

Ingraham and Marier (*6*) measured the rate of absorption of SO_2 from a 2:1 SO_2/O_2 mixture by MnO_2, Mn_2O_3, and Mn_3O_4 at temperatures between 573 and 723 K. The weight gain vs. time curves for MnO_2 show that following a rapid increase in weight, the rate of reaction decreases rapidly. In no case was more than 10% of the MnO_2 sulfated. By contrast, the weight gain increased almost linearly with time for both Mn_2O_3 and Mn_3O_4. Based on the initial rates, an activation energy of 12 kcal/g mol (5.03×10^7 J/kg mol) was estimated for MnO_2, 19 kcal/g mol (7.96×10^7 J/kg mol) for Mn_2O_3, and 21 kcal/g mol (8.80×10^7 J/kg mol) for Mn_3O_4.

Li et al. (*7*) tested fixed bed absorption of SO_2 from a 0.4% SO_2–99.6% N_2 mixture by various forms of MnO_2 and Mn_2O_3 and found significant effects of solid characteristics on absorption capacity. The absorption capacity of the oxide increased with increasing surface area and decreasing specific gravity.

Uno et al. (*3*) presented an empirical equation for the overall rate of SO_2 absorption from flue gas by an activated manganese oxide ($MnO_x \cdot i\text{-}H_2O$: $x = 1.5$–1.8, $i = 0.1$–1.0), the absorbent used in the DAP-Mn process developed by Mitsubishi Heavy Industries. The effect of temperature (373–453 K) on absorption was negligible. Generally, the reaction rate decreased with increase in $MnSO_4$ content in the absorbent and dropped sharply when the $MnSO_4$ content reached about 30–40%.

A number of mathematical models (*8, 9*) have been proposed for noncatalytic gas-solid reactions of the type similar to the absorption of SO_2 by manganese oxides. However, these models have ignored the effects of changes in solid structure during reaction which were observed in the same studies.

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Cunningham and Calvelo (*10*) developed an approximate method to take into account the influences of surface area and porosity on the reaction rate.

The objective of the present study was to generate kinetic data on the sulfation of $MnO_{1.88}$, an oxide shown to have unusually high absorption capacity for SO_2 (*7*), and to develop an adequate kinetic model for the process.

Theory

The absorption of sulfur dioxide by manganese dioxide can be described by the stoichiometric equation

$$SO_2 + MnO_2 \rightarrow MnSO_4 \qquad (1)$$

or symbolically by

$$A(g) + S(s) \rightarrow D(s) \qquad (2)$$

Under the pseudo-steady-state assumption and isothermal condition, the conservation equations for the gaseous reactant A and a spherical pellet of the solid reactant S can be written as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_{eA}\frac{\partial C_A}{\partial r}\right) = (k_s M_S) S_{ma} C_A C_S \qquad (3)$$

$$\frac{\partial C_S}{\partial t} = -(k_s M_S) S_{ma} C_A C_S \qquad (4)$$

with the boundary conditions:

$$D_{eA}\frac{\partial C_A}{\partial r} = k_{mA}(C_{Ao} - C_{Ar_o}) \text{ at } r = r_o$$

$$\frac{\partial C_A}{\partial r} = 0 \qquad \text{at } r = o$$

$$C_S = C_S^{\circ} \qquad \text{at } t = o \qquad (5)$$

The reaction rate is assumed to be first order with respect to the gaseous reactant and proportional to the solid reacting surface area. The overall fractional conversion of the pellet, X, is given by

$$X = 1 - 3\int_o^1 \frac{C_S}{C_S^{\circ}}\left(\frac{r}{r_o}\right)^2 d\left(\frac{r}{r_o}\right) \qquad (6)$$

Consider the porous pellet to consist of uniformly distributed, small particles. The local overall porosity of the pellet, ϵ_{ov}, is related to the particle porosity, ϵ_{sp}, by

$$\epsilon_{ov} = \epsilon_{pp} + (1 - \epsilon_{pp})\epsilon_{sp} \qquad (7)$$

where ϵ_{pp} is the void fraction between particles.

By assuming that the volume of each particle remains unchanged, ϵ_{sp} can be shown to be a simple linear function of conversion

$$\epsilon_{sp} = \epsilon_{sp}^{\circ} - \beta x \qquad (8)$$

where

$$\beta = (1 - \epsilon_{sp}^{\circ})\left(\frac{M_D \rho_S}{M_S \rho_D} - 1\right)$$

The local effective diffusivity of the solid with a random pore structure was derived by Wakao and Smith (*11*) as

$$D_{eA} = \epsilon_{pp}^2 D_{pp} + (1 - \epsilon_{pp})^2 D_{pp} + \frac{4\,\epsilon_{pp}(1 - \epsilon_{pp})}{1/D_{pp} + 1/D_{sp}} \qquad (9)$$

where

$$D_{pp} = \frac{1}{1/D_{AB} + 1/D_{K,pp}}$$

$$D_{sp} = \frac{1}{1/D_{AB} + 1/D_{K,sp}}$$

Upon substitution of the expression for the Knudsen diffusivity (*12*), this may be simplified to

$$D_{eA} = \epsilon_{pp}^2 D_{AB} + [(1 - \epsilon_{pp})^2 + 4\,\epsilon_{pp}(1 - \epsilon_{pp})]\epsilon_{sp}^2 D_{K,sp} \qquad (10)$$

where

$$D_{K,sp} = 19\,400\,\frac{\epsilon_{sp}^2}{S_m \rho_{sp} \tau}\sqrt{\frac{T}{M_A}}$$

The specific surface area, S_m, of a porous particle with a pore surface to pore volume ratio of r_e is given by

$$S_m = \frac{r_e \epsilon_{sp}}{\rho_{sp}} \qquad (11)$$

If r_e remains constant and if the ratio of the reacting surface area to reacting mass, S_{ma}, is equal to the ratio of the total surface area to total mass, S_m, the reacting surface area can be related to conversion by

$$\frac{S_{ma}}{S_{ma}^{\circ}} = \frac{S_m}{S_m^{\circ}} = \frac{(\epsilon_{sp}^{\circ} - \beta x)}{(1 + C_S^{\circ} M_A x/\rho_p^{\circ})\epsilon_{sp}^{\circ}} \qquad (12)$$

Equations 3–5 can now be solved numerically in conjunction with Equations 10 and 12. The overall fractional conversion at any time can be determined from Equation 6.

Experimental

Materials. Chemical grade manganese dioxide supplied by Manganese Chemical Co. was used as the absorbent. This oxide powder was pressed into spherical pellets of 5/16, 3/8, and 7/16 in. (7.94, 9.52, and 11.11 mm) in diameter. They were then dried at about 573–673 K in an oven to increase their uniformity and hardness.

The gaseous reactant was prepared by blending nitrogen and sulfur dioxide to the desired ratio. The sulfur dioxide concentration ranged from 0.2 to 1.0 vol % and was determined by a gas chromatograph calibrated by iodometry with 0.01 M iodine and thiosulfate solution.

Apparatus. A schematic diagram of the complete setup of the experimental apparatus is shown in Figure 1. Basically, it consisted of four parts based on the following operations:

- Flow control and measurement were accomplished by means of constant differential-type flow controllers and rotameters. The rotameters were calibrated with a wet test meter to an accuracy of ±1%.
- Absorption was carried out in a reactor which was a 30-mm i.d., 750-mm long Vycor combustion tube heated by a tubular electric furnace and connected to a metal joint and a cooling glass tube. In the lower section of the reactor tube enclosed by the electric furnace, a length of about 6 in. (152 mm) was filled with 1/4 in. (6.35 mm) alumina balls, which served as a preheating zone for the gas stream. A wire basket holding an oxide pellet was suspended from the weighing

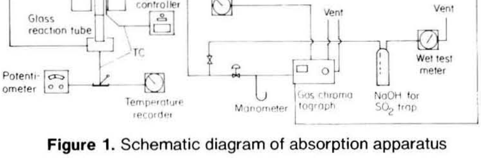

Figure 1. Schematic diagram of absorption apparatus

mechanism of the balance by a 2-mil (50 μm) nickel-chrome wire and positioned in the center of the reactor tube just above the preheating zone. The temperature of the reactor was regulated by a controller to ±1 K. A thermocouple was located near the pellet basket in the reactor, and its readings were continuously recorded. A stream of helium was admitted to the cooling tube just below the balance to protect the balance.

- Pellet weight measurement was made by a Cahn electrobalance with its recording accessories. The balance had a weighing capacity of 2.5 g, a sensitivity of 10^{-5} g, and an accuracy of ±0.5%.
- Off-gas analysis was performed by chromatography. A Beckman GC-2A gas chromatograph was used with an absorption column 6 in. (152 mm) long, ¼-in. (6.35 mm) o.d. stainless steel tube filled with silica gel. Only part of the off-gas was led to the gas chromatograph; the rest passed through a sodium hydroxide solution and then vented into the atmosphere.

Experimental Procedure. After a pellet was suspended in the reactor and the O-ring joint sealed with a clamp, the reactor was heated to the desired temperature in a nitrogen atmosphere. When the desired temperature became constant at the control point, the nitrogen was replaced by the reacting gas. The weight gain of the pellet was then recorded continuously, and gas analysis made intermittently. Reaction was continued until no appreciable weight change could be observed. At this point, the reacting gas was replaced by nitrogen.

Before each run, the balance was calibrated. The pellet was weighed, and its diameter measured with microcalipers before and after a run. About 10 measurements were made to obtain an average pellet size. Some of the reacted pellets were set in aluminum rings with Quickmount (Fisher) and then ground and polished for microscopic examination.

In a separate run, the temperature of the pellet was measured by inserting a miniature thermocouple (made by Baldwin-Lima-Hamilton Co.) into the center of the pellet. This thermocouple had a fine tip 0.014 in. (0.36 mm) in diameter. The thermocouple extension wires were used to hold the pellet in the reactor. The weight of the pellet was not measured, but the off-gas analysis was made.

Results

The flue gas from a power plant typically contains 0.2–0.4 vol % sulfur dioxide and enters the air preheater at about 573 K. Absorption runs were conducted mostly in these ranges of sulfur dioxide concentration and at temperatures from 573 to 723 K. Three pellet sizes of 5⁄16 in. (7.94 mm), ⅜ in. (9.52 mm), and 7⁄16 in. (11.11 mm) were studied. The flow rate of gas stream was so chosen that it was high enough to avoid the absorption falling into the regime of external mass transfer control but low enough to insure a stable environment for the operation of the balance. All absorption runs were maintained at a flow rate of 638 std cm³/min and conducted at atmospheric pressure.

Conversion. The manganese dioxide used had a chemical composition corresponding to $MnO_{1.88}$. On a moisture-free basis, the material contained 82.025 wt % MnO_2; the remaining oxide existed in the form of MnO. According to Bureau of Mines (*2*) x-ray analysis of their spent Mn_2O_3 after absorption in a simulated flue gas, $MnSO_4$ was the only product. In addition, Hammick (*13*) reported MnS, $MnSO_4$, SO_3, and S as the products of the reaction of MnO in SO_2. No traces of MnS were detected in our reacted samples, nor were deposits of S at colder parts of the apparatus noticed. It was therefore assumed in the present study that MnO is nonreactive and that only $MnSO_4$ is formed by absorption. The fractional conversion based on weight gain data was then calculated by means of the relationship

$$X = \frac{\text{weight gain}}{(\text{initial pellet weight})(0.82025)(M_{SO_2}/M_{MnO_2})} \tag{13}$$

Some typical fractional conversion vs. time curves are shown in Figure 2. The absorption rate, in general, increased with temperature; at a given temperature, it decreased rapidly with reaction time, and the absorption virtually stopped at a fractional conversion more than 0.6. That the conversion was not a linear function of time confirmed, as expected, that external mass transfer was not rate controlling.

Particle Characteristics. In all runs the pellets underwent little or no size change. With the pellet size remaining unchanged and pellet weight increasing as the reaction proceeded, the porosity of the pellet was expected to decrease with conversion. Table I gives the measured total pore volume by the nitrogen adsorption technique of unreacted and reacted pellets at different conversion levels. The measured porosity decreases linearly with overall conversion and can be represented by

$$\epsilon_{\text{expt}} = 0.209 - 0.375\,X \tag{14}$$

Table II shows the specific surface area measured by the BET technique with nitrogen or krypton as the absorbate at liquid nitrogen temperature. The specific surface area at a given conversion relative to that at zero conversion is plotted against conversion in Figure 3. $\bar{S}_m/\bar{S}^\circ_m$ decreases to almost zero

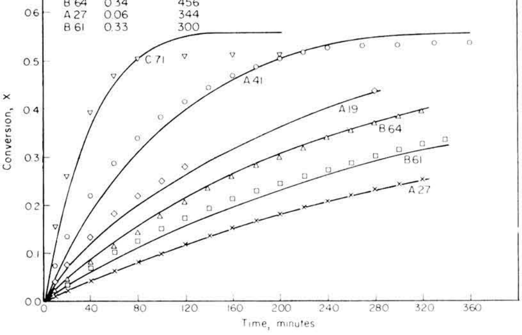

Figure 2. Fractional conversion vs. time

Table I. Total Pore Volume Measurement (by Nitrogen Adsorption)

Sample	A45	A26	A51	A41
Vol % SO_2	. . .	0.060	0.558	0.575
Reaction temp, K	. . .	566	573	673
Pellet wt, mg	560.9	614.2	674.2	731.8
Pellet diam, mm	9.35	9.45	9.36	9.71
Initial wt, mg	560.9	531.9	528.4	556.0
Pellet vol, cm³	0.428	0.442	0.430	0.480
Fract conv	0	0.256	0.460	0.538
Pore vol, cm³/g	0.144	0.0805	0.0225	0.0046
ϵ_{expt} [a]	0.188	0.112	0.0353	0.0070
ϵ°_{ov} [b]	0.721	0.744	0.738	0.753

[a] ϵ_{expt} = measured pore volume/pellet volume. [b] ϵ°_{ov} = 1 − bulk density of pellet/chemical density of solid.

Table II. Specific Surface Area Measurement

Sample	Temp, °C	Conv	S_m, m^2/g	$\bar{S}_m/\bar{S}^\circ_m$ [a]
A41	. . .	0	43.7	. . .
A42	. . .	0	45.8	. . .
A43	. . .	0	45.7	. . .
A50	. . .	0	44.7	. . .
A51	. . .	0	41.7	. . .
A52	. . .	0	41.6	. . .
B54	. . .	0	40.0	. . .
B53	. . .	0	37.2	. . .
A51	300	0.234	17.6	0.414
A26	293	0.256	13.0	0.306
A41	400	0.287	14.6	0.343
A50	300	0.349	10.4	0.244
A51	300	0.460	3.55	0.0834
A41	400	0.538	0.44	0.0103

[a] Av $\bar{S}^\circ_m$ (before reaction) = 42.5 m^2/g.

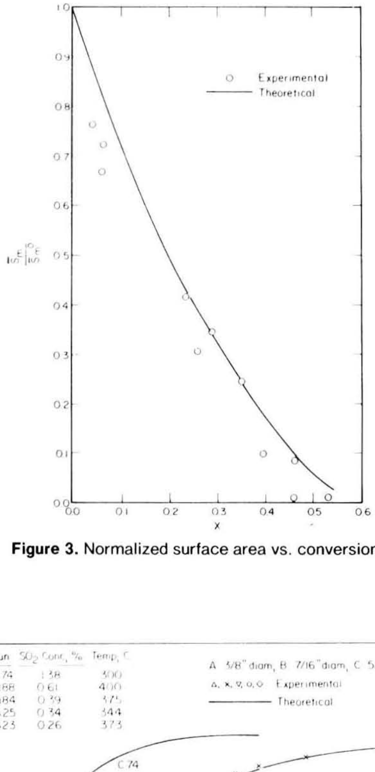

Figure 3. Normalized surface area vs. conversion

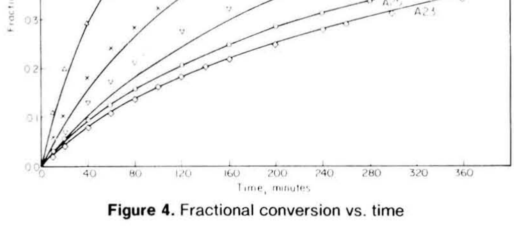

Figure 4. Fractional conversion vs. time

when conversion reaches 55%. This may well explain why absorption stops at about 60% conversion.

Fitting of Model to Data. Application of the model described in the Theory section requires a knowledge of the local properties of the pellet. Since local properties were not measured, it becomes necessary to make approximations based on relationships for mean pellet properties.

In view of the fact that pores larger than 0.05 μm do not contribute to the pore volume measured by the nitrogen adsorption technique, it is reasonable to assume that the measured porosity is that of particles only. It then follows from Equation 14 that

$$\bar{\epsilon}_{sp} = \frac{0.209}{1 - \bar{\epsilon}_{pp}} - \frac{0.375}{1 - \bar{\epsilon}_{pp}} X = \bar{\epsilon}^\circ_{sp} - \beta X \tag{15}$$

If the void fraction between particles remains unchanged with reaction, writing Equation 7 for the pellet as

$$\bar{\epsilon}_{ov} = \bar{\epsilon}_{pp} + (1 - \bar{\epsilon}_{pp})\bar{\epsilon}_{sp} \tag{7a}$$

and combining with Equation 15 give at zero conversion

$$\bar{\epsilon}^\circ_{ov} = \bar{\epsilon}_{pp} + 0.209 \tag{16}$$

With the initial overall porosity, $\bar{\epsilon}^\circ_{ov}$, estimated from the chemical density of the oxide powder and the pellet volume, $\bar{\epsilon}_{pp}$, $\bar{\epsilon}^\circ_{sp}$, and $\bar{\epsilon}_{sp}$ can then be calculated from Equations 15 and 16.

Equation 12 applied to the entire pellet may be written as

$$\frac{\bar{S}_{ma}}{\bar{S}^\circ_{ma}} = \frac{\bar{S}_m}{\bar{S}^\circ_m} = \frac{(\bar{\epsilon}^\circ_{sp} - \beta X)}{(1 + C^\circ_S M_A X/\rho^\circ_p)\bar{\epsilon}^\circ_{sp}} \tag{12a}$$

The specific surface area decreases with conversion. The relationship between $\bar{S}_m/\bar{S}^\circ_m$, and conversion predicted from Equation 12a based on the pellet properties of Run A41 is shown in Figure 3. The demonstrated agreement with experimental data lends some support to the physical picture of the porous solid proposed in the model. Although the assumption that $S_{ma} = S_m$ cannot be substantiated, it may be regarded as a fair approximation.

In the proposed model, both the local reacting surface area and effective diffusivity are considered as functions of local pellet characteristics and conversion. The numerical values of local particle porosity and local specific reacting surface area were obtained from Equations 12a, 15, and 16 by substituting the local fractional conversion for the overall fractional conversion. The assumptions made here are that the variations of local properties with conversion follow the same relationships as those for mean pellet properties, and that the initial local and initial mean pellet properties are equal. The external mass transfer coefficient was evaluated from the Ranz and Marshall correlation (*14*). The SO_2 concentration in the bulk gas phase was taken to be that of the inlet gas stream. The only parameter in the model left to be determined is the reaction rate constant.

A numerical method employing the Taylor expansion series was used to solve the system of equations in the proposed model. The reaction rate constant for each run was so chosen that the predicted conversion curve fitted most of the data points. Some typical results are shown in Figures 2 and 4. The agreement between the predicted conversion and the data points is good for most of the runs, indicating that the proposed structure of the solid is quite adequate, and that the relationships of porosity and reacting surface area with conversion are essentially correct. Derivations for individual runs range from 3 to 22%, and the average for all runs is 11%. In only a few runs, the predicted conversion curves fit most of the initial points but show a higher conversion in the final stages. The disagreement in the final reaction period seems to indicate that some parameters used in the model may not have the correct values. This is illustrated for Run C74 in Figure 4. The initial particle porosity estimated by the empirical correlation is 0.45, and the predicted final conversion is 55%, which is considerably higher than the experimental value of 46%. When the initial particle porosity is taken as 0.41 and the rest of parameters are evaluated accordingly by the normal procedure, the predicted conversions, as shown by the dashed line, are brought to closer agreement with the data.

An Arrhenius plot of the rate constant is shown in Figure 5. Although the points are scattered, a consistent temperature dependence is noted. This spread of rate constants may be attributed to the inherent nonuniformity of the initial local structure within the pellet or uncertainties in the assumptions used for estimating solid properties.

A least-squares fit of the Arrhenius equation yields an activation energy of 10.3 ± 0.8 kcal/g mol ($4.3 \pm 0.3 \times 10^7$ J/kg mol).

Justification of Model. The proposed model fits the experimental data quite well in the temperature range studied. Moreover, the experimental measurements of the specific surface area and porosity confirmed the theoretical predictions of their variations with conversion. Further evidence in support of the model may be obtained by microscopic examination of the reacted pellets. In particular, the sulfur distribution in the pellet, as detected by a scanning electron microscope, may provide a more critical test.

Figure 6 shows that the agglomerated particle size ranges from 2 to 30 μm. The voids between agglomerated particles appear wider than 1 μm. The unreacted pellet, as shown in Figure 6, has an average specific surface area of 42.5 m^2/g. If it is assumed that all the surface area is contributed by small, uniform-sized, spherical, impervious grains, the grain would have a diameter of 0.03 μm. For Run A41, the measured specific surface area of the reacted pellet is 0.44 m^2/g. The grain size based on the above assumption would be about 4 μm. As the conversions of A41 and C87 are about the same, the grain or particle size of sample C87 should be on the order of microns. This is approximately true as shown in Figure 7. Thus, the assumption that the measured pore volume represents the porosity of particles, which decreases to virtually zero when conversion reaches about 55%, appears to be valid.

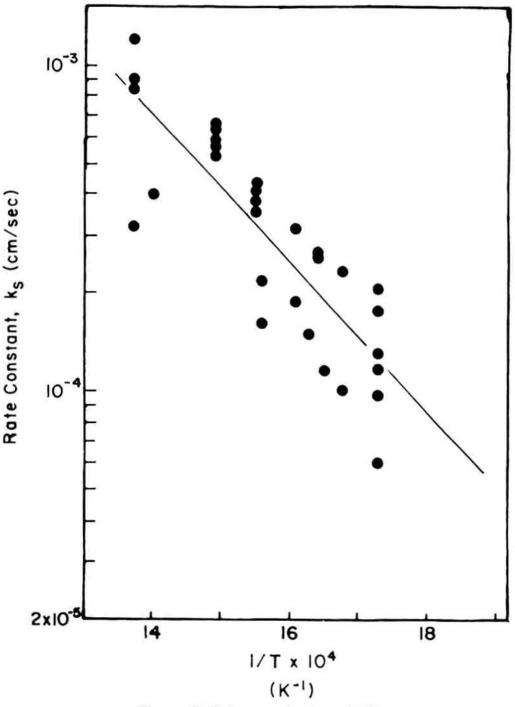

Figure 5. Rate constant vs. $1/T$

Comparison of Figures 6 and 7 shows that the reacted sample is distinguished from the unreacted sample by a rougher surface. In Figure 7a, the micrograph was taken at a location close to the center of the pellet, and in Figure 7b, near the edge of the pellet. From these two pictures, it is clear that reaction at 673 K occurred throughout the particle. The same behavior was observed at 573 K.

Identification of sulfate in the particle was made by determining the relative quantities of sulfur that existed in the probe area of an electron beam. In Figure 8 the magnitude of a particular number indicates the relative quantity of sulfur in the shaded area probed by the electron beam. A slight

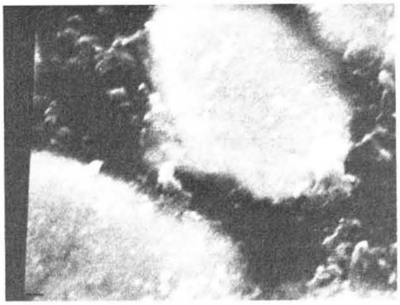

Figure 6. MnO_2 pellet, 6000× (1 mm = 0.16 μm, $X = 0$)

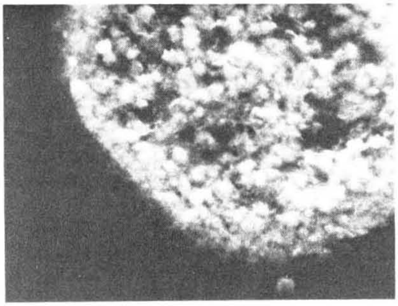

Figure 7a. Run C87, center, 6000× (1 mm = 0.16 μm, 673 K, $X = 0.506$)

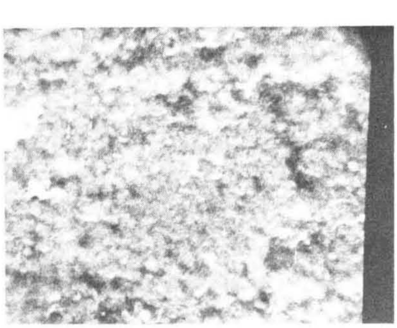

Figure 7b. Run C87, edge, 6000× (1 mm = 0.16 μm, 673 K, $X = 0.506$)

variation of the numbers from the edge to the center of the pellet could be caused by differences in local porosity. This was shown by the fact that a much larger number was obtained when the electron beam was directed at an area where local porosity was much smaller because of lack of large voids or cracks. Nevertheless, the numbers in Figure 8 indicate that the sulfate was distributed throughout the pellet. This provides further evidence for the nontopochemical behavior of the reaction on the pellet level. The assumed first order kinetics with respect to SO_2 was supported by the nearly linear relationship between the initial reaction rate ($r_o\, dX/dt$) and bulk gas concentration (C_{AO}).

The solid and gaseous reactant concentration profiles in the reacted pellet at different conversion levels predicted by the model for Run C87 are shown in Figure 9. The solid lines represent the dimensionless solid reactant concentration profiles, and the dashed lines the dimensionless gaseous reactant concentration profiles at indicated conversion levels. At low conversion the gaseous reactant diffuses only a short distance into the pellet, and most of the reaction takes place near the surface of the pellet. As more solid is reacted, the gas penetrates deeper into the pellet. Finally, both the gaseous and solid reactant concentration profiles become almost flat. Thus, the model predicts the same type of sulfur distribution for C87 as observed by the scanning electron microscope. Concentration profiles for Run C74 at 573 K predicted by the model (Figure 10) also indicate that the final sulfur distribution in the particle was nearly uniform.

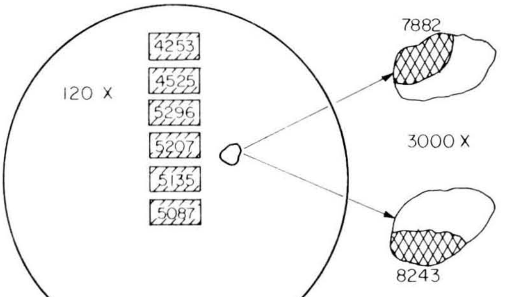

Figure 8. Sulfur distribution, Run C87 (673 K, $X = 0.506$)

Discussion

The proposed model represents the data satisfactorily in the temperature range from 573 to 723 K. Close agreement between the model and the data for most of the runs indicates that the pore structure, porosity, and reacting surface area of the solid reactant are adequately described by the model. The small discrepancy between the model and data for a few runs may possibly be caused by factors such as variation in bulk gas concentration, nonuniform solid temperature, pore structure, and solid surface.

In the model the inlet concentration of SO_2 was taken as the concentration of the bulk phase. For a typical run at 673 K (Run B62, 0.33% SO_2), the off-gas concentration was approximately 32% smaller than the inlet concentration during the first 5–15 min. The difference dropped to 25% after 1 h and to 8% after 3 h. Although a concentration difference could exist along the surface of the pellet, it would be smaller than the observed difference between the inlet and exit gas. It seems reasonable to neglect the effect of concentration variation in the bulk phase.

The maximum center temperature rise of a pellet at a relatively fast reacting condition (1.44% SO_2 and 573 K) was observed to be only 3 K in the first hour of reaction. Furthermore, the Anderson criterion (*15*) may be used to test the validity of the isothermal assumption by using the initial rate of an almost identical run (Run C74, 1.38% SO_2 and 573 K). The Anderson criterion for isothermal condition is given by

$$\frac{(-\Delta H_r)R_A^\circ r_o^2}{T_{r_o}k_T} < \frac{3T_{r_o}}{4\Delta E_a} \qquad (17)$$

where T_{r_o} is the surface temperature (K), k_T the thermal conductivity (cal/s cm K), and ΔE_a the activation energy divided by gas constant (K). For Run C74, $-\Delta H_r = 57\,700$ cal/g mol, $r_o = 0.388$ cm, $T_{r_o} = 573$ K, $\Delta E_a = 5180$ K, $R_A^\circ = 2.5 \times 10^{-6}$ g mol/cm^3 s, and $k_T = 0.00409$ cal/s cm K. Substitution of these values into both sides of Equation 17 yields

$$9.3 \times 10^{-3} < 8.3 \times 10^{-2}$$

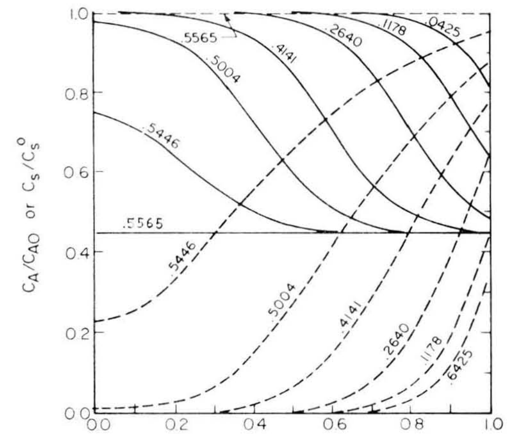

Figure 9. Solid and gas reactant concentration profiles of Run C87, 673 K

— C_S/C_S°
- - - C_A/C_{AO}
Parameter: *X*

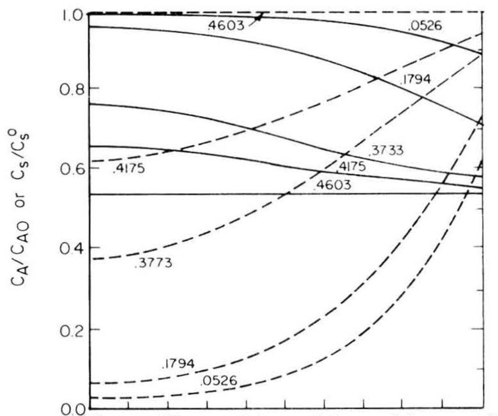

Figure 10. Solid and gas reactant concentration profiles of Run C74, 573 K

— C_S/C_S°
- - - C_A/C_{AO}
Parameter: *X*

Since Anderson's criterion is satisfied, the isothermal assumption may be considered valid, and the nonuniform solid temperature, if present, is not likely to be a factor in the discrepancy.

The model considers a pellet to consist of porous particles whose size remains unchanged during reaction. The porosity of particles decreases linearly with conversion. The initial particle porosity, $\overset{\circ}{\epsilon}_{sp}$, and β were evaluated by means of Equation 15 which is an empirical correlation based on measurements of a few selected samples. With these estimated values of $\overset{\circ}{\epsilon}_{sp}$ and β, the model is in satisfactory agreement with the data for most of the runs. Although agreement is less satisfactory for some runs, it can be improved by using a different set of values for $\overset{\circ}{\epsilon}_{sp}$ and β, as has been shown for Run C74 in Figure 4. This seems to imply that the values of $\overset{\circ}{\epsilon}_{sp}$ and β may not be correctly estimated in all cases. The effects of $\overset{\circ}{\epsilon}_{sp}$ and β on the final conversion may be seen from Equation 8. When the particle porosity becomes zero, the final conversion X_f is given by

$$X_f = \frac{\overset{\circ}{\epsilon}_{sp}}{\beta} \tag{18}$$

Therefore, incorrectly estimated values of $\overset{\circ}{\epsilon}_{sp}$ and β can both lead to an erroneous prediction of the final conversion.

The influence of $\overset{\circ}{\epsilon}_{sp}$ and β on the reacting surface area can be seen by noting Equation 12 which shows S_{ma} to depend on $\beta/\overset{\circ}{\epsilon}_{sp}$. Since the reaction rate is assumed to be proportional to reacting surface area, a different value of $\beta/\overset{\circ}{\epsilon}_{sp}$ will vary the course of reaction.

Initial nonuniform pore structure within a pellet, a likely occurrence, could contribute a further effect on the reaction rate. If, for example, the peripheral particles had a higher initial porosity than the interior particles, the actual reaction rate would be much higher than the predicted rate based on the mean value of particle porosity.

From the above discussion, it is believed that the discrepancy between the model and data for some runs is largely attributable to the incorrect values of the initial particle porosity, the initial nonuniform pore structure of the pellet, or both.

Ingraham and Marier (*6*) reported the initial rate for the reaction of MnO_2 with a 2:1 mixture of SO_2 and O_2 as given by

$$\log \overset{\circ}{R}_A = 4.588 - 2.587 \times 10^3/T \tag{19}$$

where $\overset{\circ}{R}_A$ is in the units of mg/cm^2 min. At 673 K, the initial rate calculated from this equation is 5.6 mg/cm^2 min, and the initial rate observed for Run C71 in this work is 1.6 mg/cm^2 min. The SO_2 concentration in Run C71 was 1.0%. Taking the concentration difference into account, the two rates are comparable. Also, the values of activation energy obtained from Ingraham and Marier's data (12 ± 1 kcal/g mol) and this work (10.3 ± 0.8 kcal/g mol) are very close. This seems to show that the reaction kinetics might be the same in both cases. Ingraham and Marier's data indicated that reaction stopped completely before the conversion reached 10%. Since their pellets were very dense, the reaction would be expected to stop at a conversion level lower than found in the present work.

Conclusion

A nontopochemical model has been proposed for the kinetics of sulfur dioxide absorption by a porous spherical pellet of chemical grade manganese dioxide. The spherical pellet of manganese dioxide is assumed to consist of porous particles whose size remains unchanged during reaction. Equations have been derived to relate the particle porosity and the ratio of reacting surface area to reacting mass to fractional conversion. Calculation of effective diffusivity is based on Wakao and Smith's random pore model. The reaction is assumed to be irreversible and first order with respect to gas concentration, and also proportional to the reacting surface area.

The experimental data were well represented by the proposed model. The nearly uniform distribution of $MnSO_4$ in the pellet predicted by the model at the end of reaction was confirmed by scanning microscopic observations. The close agreement between predictions and data indicates that the variations of the particle porosity and reacting surface area with conversion are adequately described by the model.

An activation energy of 10.3 ± 0.8 kcal/g mol was obtained from an Arrhenius plot of rate constants. It compares favorably with the value of 12 ± 1 kcal/g mol based on initial rates reported by Ingraham and Marier.

The proposed model may therefore be recommended for SO_2 absorption by manganese dioxide in the temperature range of 573–723 K. Application of the model requires only knowledge of the initial specific surface area and initial porosities of the pellet and particles.

The temperature range (573–723 K) and SO_2 concentration range (0.2–1.0 vol % SO_2) studied in this work are of practical interest to pollution control of sulfur dioxide emission.

Nomenclature

A, S, D = reaction components
C_A = gas reactant concentration, g mol/cm^3
C_{AO} = gas reactant concentration in bulk gaseous phase, g mol/cm^3
C_{Ar_o} = gas reactant concentration at pellet surface, g mol/cm^3
C_S = solid reactant concentration, g mol/cm^3 pellet
D_{AB} = molecular diffusivity, cm^2/s
D_{eA} = effective diffusivity, cm^2/s
D_K = Knudsen diffusivity, cm^2/s
D_{pp} = diffusivity defined in Equation 9, cm^2/s
D_{sp} = diffusivity defined in Equation 9, cm^2/s
k_s = rate constant, cm/s
k_{mA} = mass transfer coefficient, cm/s
M = molecular weight
r = radius, cm
r_e = ratio of pore surface to pore volume, cm^{-1}
r_o = pellet radius, cm
R_A = reaction rate, g mol/cm^3, s
S_m = specific surface area of solid, cm^2/g
S_{ma} = reacting surface area to reacting mass ratio, cm^2/g
T = temperature, K
t = time, s
X = overall fractional conversion
x = local fractional conversion
$\overline{}$ = mean property

Subscripts

A = gas reactant
D = solid product
f = final stage of reaction
ov = overall property of pellet
p = pellet
pp = between particles
sp = particle
S = solid reactant

Superscript

$\circ$ = initial condition

Greek Letters

β = defined in Equation 8
ϵ = porosity
ρ_S, ρ_D = chemical density of S and of D, g/cm^3
ρ_p, ρ_{sp} = density of pellet and of particle, g/cm^3
τ = tortuosity, assumed to be two

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Thin-Layer Chromatographic Technique for Identification of Waterborne Petroleum Oils

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■ A thin-layer chromatographic procedure for the identification of waterborne petroleum oil pollutants for use in either the laboratory or the field is developed. Aromatic and polar compounds are removed from the oil sample by a liquid-liquid extraction with acidified methanol. The extract is then chromatographed on a silica-gel thin-layer plate. Separated components are detected by their fluorescence under long and short wave ultraviolet light. Iodine staining is also used to visualize unsaturated, nonfluorescing compounds. This procedure is successfully applied to "fingerprinting" gasolines, kerosines, diesel oils, heavy fuel oils, lubricating oils, and ship bilge oils.

The feasibility of using thin-layer chromatography (TLC) to identify the source of an oil spill was investigated. Originally, it was thought that a quick, simple technique such as the spot chromatography of petroleum oils used by Schulinder (*1*) might be of use as a fast screening technique to narrow the range of possible suspect sources for an oil spill. The screening technique would have been used primarily as a method of excluding improbable suspect samples on the basis of qualitative differences between the TLC signatures of suspects and the spill sample. It soon became apparent, however, that visual examination of the oil samples themselves, noting such factors as color and viscosity, provided as much information as the simple spotting of oil on paper and examination under ultraviolet light.

A more informative technique for the systematic chromatographic identification of petroleum oils was developed by Matthews (*2*). This scheme, however, is highly complicated in that numerous TLC plate coatings and solvent systems must be employed. Furthermore, only elementary separation is achieved on plates that are badly streaked. This, at best, provides very little identification unless the samples are not closely related chemically.

Our preliminary work established that the resolving power of TLC to separate fluorescing compounds found in oils was very poor when the oil, or a dilution of the oil, was spotted directly on the TLC plate. Presumably, this is due to the overwhelming complexity of the mixture of compounds generally present in oils. Furthermore, it revealed that only those compounds capable of at least some resistance to chemical alteration due to weathering should be considered. In addition, a simple visualization process such as black light illumination was considered more desirable than more involved techniques such as sulfuric acid charring. For these reasons, a preliminary fractionation of the starting material was developed; polycyclic aromatic compounds, hetero and polar compounds (N, O, and S containing) were isolated from oils and chromatographed. Although these compound types have some solubility in water (and could diffuse into the aqueous layer from an oil spill on water) (*3*) and are subject to oxidative loss of fluorescence, they have provided a satisfactory TLC fingerprint of oils.

Materials and Methods

Sample Preparation. One ml of oil sample is placed into a 15-ml centrifuge tube with 1 g of color-tagged anhydrous calcium sulfate. The mixture is then shaken on a vortex mixer for 1 min. If the color indicator is not visible at the end of 1 min, an additional gram of calcium sulfate is added and the sample is remixed. One ml of 0.4% glacial acetic/methanol (by volume) is added, and the mixture is again shaken for 3 min or until well emulsified. The mixture is then centrifuged for 10 min at 2500 rpm. The methanolic phase is withdrawn and placed in a stoppered 5-ml glass vial. If the sample is a light distillate oil (gasoline, kerosine, jet fuel, or a #1 fuel oil), it is necessary to concentrate the methanol extract. This is accomplished by placing the vial containing the extract on a hot plate at 65 °C with a Pasteur pipet suspended about 1 cm above the liquid surface. A vacuum is applied to the pipet until fine oil droplets precipitate out of solution.

Development of Plate and Visualization. Five microliters of the methanolic extract is spotted along the lower edge of an *unactivated* 20 × 20 cm TLC plate (Adsorbosil 1 or 5, Applied Science Laboratory) with a Camag spotting guide. A Camag Vario-KS chamber is used to carry out development of the TLC plate horizontally in an unsaturated atmosphere. To achieve reproducibility of Rf values from laboratory to laboratory, it is necessary to standardize the water content of the adsorbent. This is done by placing the TLC plate adsorbent side down on the developing chamber and allowing it to precondition for 45 min over a glass tray containing 65% sulfuric acid/water (by volume). This results in uniformly deactivated plates. Preconditioning is stopped by sliding a stainless steel sheet in between the sulfuric acid tray and the face of the TLC plate. The sulfuric acid tray is then removed and replaced with a tray containing 10% acetic acid/methanol (by volume). An area 20 cm wide and 2 cm high on the TLC plate (located just above the spotted sample) is preconditioned by exposing the thin-layer plate to the methanol vapor by sliding out the stainless steel divider 2 cm (Figure 1). After 5 min the methanolic conditioning is stopped. This procedure establishes a methanol deactivated zone 2 cm wide across the bottom of the plate.

The solvent reservoir is filled with 4% methanol/hexane (by volume), and development is started when the solvent wick is brought in contact with the adsorbent. Development is allowed to continue for 45 min (about 15-cm solvent migration). The plate is then removed from the developing chamber and allowed to air dry before it is visualized under long (365 nm) and short (254 nm) wavelength ultraviolet light. After UV light inspection and photographic documentation, the plate is exposed to iodine vapor in an airtight bell jar and then reinspected. The chromatograms are photographed with Kodachrome 25 color film in a Pentax 35-mm single-lense reflex camera. The fluorescence on the plate is recorded using multiple exposure times of 1.5, 2.0, and 2.5 s at f-1.4. After iodine staining, the chromatograms are rephotographed using transmitted daylight and adjusting the f-stop and shutter speed setting accordingly.

Discussion

This chromatographic technique is used primarily as a means of assessing a match or mismatch between an oil spill sample and suspect oil samples solely by visual examination of their thin-layer chromatograms under UV light and iodine staining. Generally, black light inspection yields more information than iodine staining, and this sole visualization technique is generally conclusive. However, some oils, such as hydraulic fluids and some lubricating oils, contain an appreciably lower aromatic hydrocarbon content, while generally possessing unsaturated stabilizers and antioxidants (*4*). Visualization of these nonfluorescing additives is accomplished with the iodine staining technique.

The acidified methanol extract of petroleum oils contains not only light aromatic hydrocarbons and unsaturated, nonfluorescing additives, but also very heavy, polar compounds. As a result, the use of a relatively nonpolar developing solvent leaves many polar fluorescing compounds at the starting position, yet provides good separation of the lighter (1–3 fused ring) aromatics. Conversely, the use of a strong eluting solvent provides good separation of all the heavy polar components but runs all the light and medium aromatics together in a brightly fluorescing band at the solvent front. This situation necessitated the use of the methanolic preconditioning gradient across the face of the plate. Furthermore, because all components of the extract are soluble in the preconditioning solution, development of the plate begins with the entire sample migrating quickly across the methanol preconditioned zone and concentrating in a narrow band, rather than a circular spot, at the far edge of this zone. The components which separate out on the TLC plate therefore retain this band shape; consequently, close-running compounds are much more highly resolved. However, actual chromatographic separation begins to occur only at the far edge of the methanol preconditioned zone, where a steep methanol gradient in the adsorbent layer has been established (Figure 2).

Zeeuw (5) states that in some cases the use of unsaturated chambers, particularly with complex mixtures of closely related substances, produces better separation than saturated chambers. The use of a vapor-saturated tank atmosphere produced extreme tailing of oil components. For this reason, unsaturated conditions were utilized. Furthermore, Zeeuw (*6*) has established that in order to control vapor diffusion of the developing solvent, careful attention must be paid to the thickness of the air space directly below the adsorbent. Optimum separation of fluorescing bands was achieved by carefully limiting the volume of space between the plate surface and the tank wall by using a properly spaced seal (the raised edge stainless steel Camag divider). This results in a developing technique which allows solvent vapor to travel in only one direction across the plate (in the space just below the adsorbent surface) in the same direction as the moving solvent front.

Controlled Testing

This chromatographic technique for the identification of waterborne petroleum oils was control tested and evaluated on 10 simulated oil spill cases. These tests consisted of one or more spill samples which were weathered between 2 and 96 h. The various types of oils ranged from lube oils, crudes, and kerosines to bunkers and heavy fuel oils. In all cases, the same general type of suspect oils was provided in the same spill case, i.e., if the spilled oil was a No. 2 fuel oil, then only No. 2 fuel oils were provided as possible suspects. The logistics team for these simulated spills and the analytical teams for infrared spectroscopy, fluorescence spectroscopy, gas chromatography, and thin-layer chromatography were independent groups (*7*). The results of these tests are shown in Table I. In all cases where unique correlations were assigned by TLC (positive match between spill and suspect), these matches were correct. Table II illustrates that the apparent error in the TLC oil matching procedure exists in assigning a negative correlation where a unique correlation is known to exist. The cause of the high percentage of negative correlations was traced to TLC's sensitivity to contamination extractable from the solid substrates used in the oil spill testing.

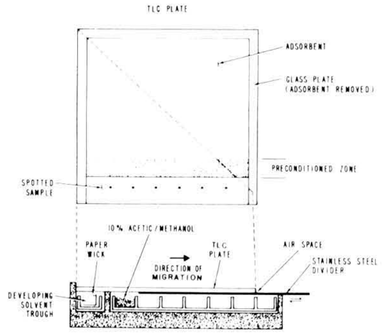

Figure 1. Longitudinal section of developing chamber

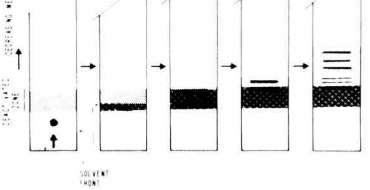

Figure 2. Sequence of sample development utilizing vapor preconditioning and preconditioning zone

It became apparent that the extraction technique outlined above removed both fluorescing and polar compounds not only from the oil, but also from the solid substrates. Sand samples were collected from several area beaches and extracted with 0.4% acetic acid in methanol. Residual oil was found in some of the sand samples indicating either chronic long-term pollution or a possible recent pollution incident. Sawdust was similarly collected and extracted. In each case, fluorescing bands were detected in the extracts. The source of the bands extracted was not determined; however, it seems possible that the lubricant used on the power saw could be responsible. Soil and vegetation samples were also investigated for possible extractable contaminants. Only a small percentage of these samples showed contamination. Nevertheless, this demonstrated that vegetation and soil are also possible sources for the introduction of contaminants to the thin-layer chromatogram of an oil which comes into contact with these substrates.

Table I. Correlation of 10 Simulated Spills by TLC

Spills prepared by independent team 35 source oils	Correlations (124 data points) Possible	Obsd	
1: 3 crudes	43	24	Unique
2: 2 #2 fuel oils	0	1	Probable
3: 4 #2 diesel oils	81	99	No correlation
4: 4 #4 fuel oils			
5: 3 #5 fuel oils			
6: 5 bilge oils			
7: 3 jet fuels			
8: 3 motor oils			
9: 4 hydraulic fluids			
10: 4 lubricating oils			

Results

78 correct responses

46 incorrect responses

0.629 probability of success

$\left(\frac{\text{No. of correct responses}}{\text{Total possible responses}}\right)$

Exposure

2 h to 4 days
on seawater,
sand, sawdust,
dirt, and vegetation

Table II. TLC'S Ability to Uniquely Correlate Spill Samples on Various Substrates from 10 Simulated Spill Cases

Spill samples	No. of unique correl poss	No. of prob or neg correl obsd	Causes
Oil on saltwater	9	1	Inability to distinguish two crudes from same oil field
Oil on sand	9	4	Oil contaminated sand
Oil on sawdust	4	4	Compounds extracted from sawdust substrate
Oil on vegetation	4	1	Polar compounds and lipids extracted from vegetation
Oil on dirt	1	0	
Mixture of 2 oils (suspect)	3	3	Lost identity (Oil A + Oil B = Oil C, not Oil A + B)

Table III. TLC Correlations of 10 Simulated Spills on Salt Water Substrates (Adjusted for Limitations)

Correlations Possible	Obsd		Results
9	9	Unique	31 correct responses
0	1	Probable[a]	1 probable correlation
23	22	No correlation	0.968 probability of success
			$\left(\frac{\text{No. correct responses}}{\text{Total possible responses}}\right)$

[a] 2 Kuwait crudes from the same field.

In addition, Table II shows that whenever a mixture of two or more oils is encountered, no correlation of the resulting mixture to any of the "ingredient" oils is possible. When two or more oils are mixed, the identities of the individual mixed oils are lost, and a new and distinctly different oil is formed. This situation will always produce a negative correlation by the present TLC System.

The incorrect responses shown in Table II gave an indication that TLC's reliability could be greatly improved if certain limitations were placed on its use. Table III shows the results after all samples on solid substrates and mixtures of oils from different sources were excluded. Of a possible nine correlations between a spill sample on water and the correct unweathered suspect oil, nine correct assignments were made.

The one probable correlation was found between two Kuwait crudes supplied by different oil companies but coming from the same oil field. Numerous analytical techniques (including mass spectroscopy) were employed as well as computer analysis of the data; no significant differences could be found between these two oils. Nevertheless, this probable response was scored as an incorrect answer, due to inability to distinguish between these two crudes. The resulting probability of attaining a correct spill/suspect match becomes 0.968.

Results

The TLC system was applied to actual oil spill cases. Table IV compares the analytical results of gas chromatography, infrared spectroscopy, fluorescence spectroscopy, and thin-layer chromatography in 20 real world spill cases. These data show that in 45% of the spill cases ($N = 9$), all four techniques agreed. Furthermore, at least three of these techniques agreed 73% of the time. These comparable results for all four techniques clearly show that the TLC procedure is not demonstrably different from the other chromatographic or spectroscopic oil analyses.

Figure 3 is a short wavelength UV light photograph of the chromatogram of an actual oil spill case. The spill and all suspect samples were obtained on 11 October 1974 in Boston, Mass. Seven suspect samples were tugboats moored at a Fleet tug dock; all samples were taken from the engine room or aft bilges of these boats. The spill sample was taken from the surface of the water near the tugboat dock. Inspection of the chromatograms (Figure 3) shows suspect No. 1 and the spill to be visually identical.

After UV light inspection the TLC plate was exposed to iodine vapor. Figure 4 is a daylight photograph of the plate. Only suspect No. 1 and the spill chromatogram are identical. These results were verified by fluorescence, infrared, and gas chromatographic analyses.

Table IV. Comparison of Percentage of Agreement[a] Among Thin-Layer Chromatography, Gas Chromatography, Infrared, and Fluorescence Spectroscopy in 20 Actual Oil Spill Cases

	TLC	GC	IR	Fluor
4 Agree	45	45	45	45
3 Agree	30	15	30	35
2 Agree	15	20	15	10
1 Alone	10	20	10	10

[a] Agreement constitutes one of three responses: match, inconclusive, and mismatch.

Figure 5 is a UV light photograph of a second spill case. Samples 1, 2, 4, and 5 were taken from the surface of the Rahway River, New Jersey, from sampling locations about ½ mile apart. One suspect sample (3) from a leaking fuel oil tank valve was also taken. All spill samples are chromatographically identical, indicating that the oil had spread a considerable distance down river. The chromatogram of the fuel tank sample matches the river spill samples. These results were again verified by fluorescence, infrared, and gas chromatographic analyses.

This TLC procedure for the identification of oils was set up at the U.S. Coast Guard Captain of the Port (COTP) Philadelphia. The Pollution Control personnel at this Coast Guard facility have investigated an average of two spills every three days over the past year. Two days were spent teaching the TLC technique to the COTP personnel. They had no prior exposure in the analysis of oils. On the third day a spill of 1000 gal of a heavy fuel oil occurred. A suspect tanker was boarded, and five samples were taken. These samples were from the bunker tanks, the cargo tank, the slop oil tank, the pump room bilge, and a solvent bucket on the deck of the ship. The spill sample was taken from the Delaware River between the ship and the dock. The pollution investigators performed the TLC analysis and concluded that the spill sample and all suspect samples, except those from the bunker tank and the bucket on the ship's deck, were identical. In the face of this evidence, the master of the vessel did admit that this ship was responsible for the spill. These samples were reanalyzed. Figure 6 shows the UV light photograph of the TLC plate. The spill and samples 3, 4, and 5 are identical, all containing a very polar compound at a low Rf value which is absent in samples 6 and 1. Sample 1, from the bucket on this ship's deck, has a similar chromatogram to sample 6 and probably contains some of the oil from the bunker tank. The samples were analyzed by fluorescence, infrared, and gas chromatography techniques which verified these results.

Conclusions

This TLC procedure is presently in routine use at the Coast Guard Research and Development Center, Groton, Conn., as part of a multimethod approach to the identification of oil spills. This procedure has been applied to more than 50 actual oil spill cases in conjunction with routine infrared, gas chromatographic, and fluorescence analyses. The use of this technique in the field by inexperienced personnel, with a few hours of instruction, is possible.

By controlled deactivation of the thin-layer adsorbent and preconditioning with methanol, much improved chromatographic separation and reproducibility are possible. However, close attention must be paid to the thickness of the space directly below the adsorbent layer to control vapor diffusion.

Through a series of in-house oil spill tests, this TLC procedure demonstrated that misleading, nonmatching chromatograms could be generated between a suspect and spill sample due to extraction of contaminants from solid substrates. In addition, the technique cannot match an oil mixture to each of the "ingredient" oils.

The ability of this technique to maintain unique correlations between unweathered oils and oils weathered up to four days was demonstrated. The probability of correctly matching a spill sample to suspect by this procedure was 0.968, when it is applied to oil spill identifications within the framework of the above-mentioned precautions.

Present research is currently being carried on to improve this technique and enhance its utility. Areas such as the effect of weathering, application to hazardous materials, and oil slick integrity are being considered.

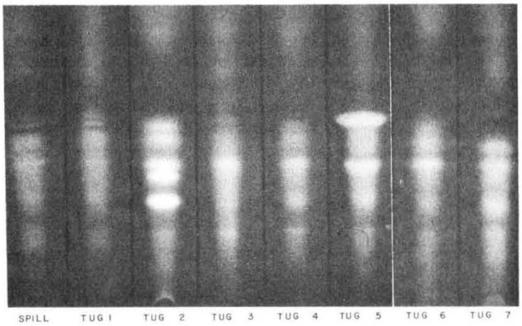

Figure 3. UV light photograph of spill and seven suspect tug samples

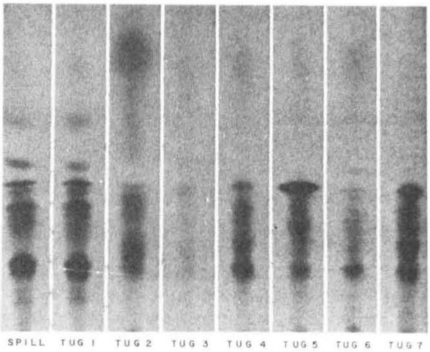

Figure 4. Iodine-stained photograph of spill and seven suspect tug samples

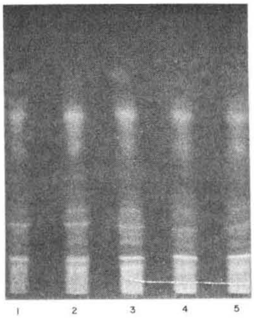

Figure 5. UV light photograph of five oil samples

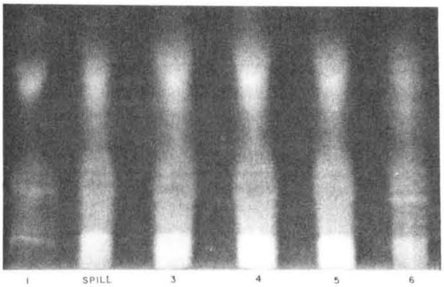

Figure 6. UV light photograph of spill and six suspect samples

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Comparison of Ozone Determinations by Ultraviolet Photometry and Gas-Phase Titration

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■ A comparison of ozone determinations based on ultraviolet absorption photometry and gas-phase titration (GPT) shows good agreement between the two methods. Together with other results, these findings indicate that three candidate reference methods for ozone, UV photometry, IR photometry, and GPT are in substantial agreement. However, the GPT method is not recommended for routine use by air pollution agencies for calibration of ozone monitors because of susceptibility to experimental error.

The absolute accuracy of ozone calibration methods has been of considerable interest to environmental chemists in recent years. Much of this activity stems from a report by Boyd and coworkers (*1*) which questioned the accuracy of the neutral-buffered iodometric method of ozone analysis. Since the latter method forms the basis of the *Federal Register* method (*2*) for calibration of ozone monitoring instruments, a number of groups have attempted to evaluate the accuracy of iodometric methods with reference to independent standards (*3, 4*). Somewhat different versions of the iodometric method previously used in California have recently been examined by the Ad Hoc Oxidant Calibration Committee (*5*) of the California Air Resources Board (CARB) and also by the Statewide Air Pollution Research Center (*6*), University of California, Riverside, Calif. (SAPRC). These studies and others (*7, 8*) show that the neutral-buffered KI method reads high by 10–30%, depending on details of the procedure.

One problem encountered in connection with the foregoing evaluations was the fact that relatively few methods for absolute ozone measurement were available, and the reliability and intercomparability of the various methods had not been well established. The principal candidate methods are ultraviolet photometry, infrared photometry, and gas-phase titration (GPT). The UV and IR methods have recently been compared in joint tests conducted by the CARB Oxidant Calibration Committee and the SAPRC group (*5, 6*). The results showed excellent agreement (within approximately 2%) between the two methods, which are completely independent.

The situation was less clear, however, with respect to the GPT method. For example, the GPT results disagreed by 9% with the UV standard in the CARB Oxidant Committee tests (*5*). Also, the GPT method was previously reported to be in good agreement with the neutral-buffered KI method (*3*), and the latter method is now known to be incorrect.

In the present work we have attempted to resolve this discrepancy by conducting further comparisons of the UV and GPT analyses. The results show good agreement between the two methods and provide further substantiation of the intrinsic accuracy of all three reference methods.

Experimental

According to the UV method, the O_3 concentration is given (in ppm) by

$$O_3(\text{ppm}) = \frac{10^6\,T}{273\,Pkl}\log\frac{I_o}{I_t}$$

where:

T = temperature, K
P = total pressure, atm
k = extinction coefficient of ozone, base 10, units $\text{cm}^{-1}\ \text{atm}^{-1}$ (STP)
l = path length, cm
I_o = intensity with carrier gas only
I_t = intensity with O_3 present

The extinction coefficient for O_3 at 254 nm has been measured by several groups (*9–14*) using a variety of physical methods to measure the O_3 concentration. Table I lists the results of these studies and the methods used.

The manometric method is based on pressure measurements of gaseous O_3, requiring in at least one case (*9*) a substantial and somewhat uncertain correction for decomposition. The method of decomposition stoichiometry depends on the pressure change which accompanies the decomposition:

$$2\,O_3 \rightarrow 3\,O_2$$

Clyne and Coxon (*13*) determined O_3 concentrations in a flow tube by means of titration with NO, so that their method was essentially equivalent to the GPT.

The value used in the present work was 135 $\text{cm}^{-1}\ \text{atm}^{-1}$, which we consider to be the preferred value on the grounds that the lower values may have been the result of O_3 decomposition.

Photometric Apparatus and Methods. There are three components to the photometric apparatus, the light source, the absorption cell, and the light detector (Figure 1). A Pen-Ray low-pressure mercury lamp (Ultraviolet Products) was used as a source of the 254-nm light. A ¼-m Jarrel-Ash monochromator was used to spectrally isolate the 254-nm line. (This component is not strictly necessary and can be replaced

Table I. Ozone Extinction Coefficient Measurements

Authors	Ref	k, cm^{-1} atm^{-1} STP, base 10	Method
Inn and Tanaka (1953)	*9*	133	Manometric
Hearn (1961)	*10*	134	Decomposition stoichiometry
DeMore and Raper (1964)	*11*	135	Decomposition stoichiometry
Griggs (1968)	*12*	132	Manometric
Clyne and Coxon (1968)	*13*	136 (250 nm)	GPT
Becker et al. (1974)	*14*	135	Manometric

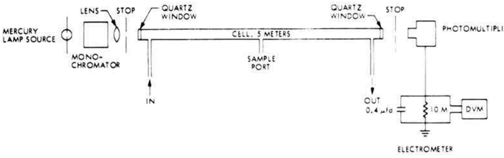

Figure 1. Schematic diagram of ultraviolet ozone photometer

by an interference filter to isolate the 254-nm line.) Collimation of the light beam was aided by use of a 25-cm focal length quartz lens. Stability of the light source was enhanced by operation from a constant voltage transformer and by enclosing the lamp in an aluminum block for increased thermal inertia. The absorption cell is constructed of 2-in. o.d. Pyrex tubing, and has a path length of 5.00 m. Quartz windows are attached at each end by means of epoxy cement, with care being taken to minimize internal exposure of cement. The 254-nm light emerging from the cell is monitored with a Hammamatsu-type R166 solar-blind, side-on photomultiplier tube. The photomultiplier is operated at 340 V. The photomultiplier output voltage is measured across a 10-MΩ resistor and is read with a four-digit voltmeter. A 0.4-μfd condenser is placed in parallel with the resistor to obtain a suitable time constant.

Ozone was generated in a stream of cylinder air by means of a photochemical generator of conventional design, employing a Pen-Ray low-pressure mercury lamp with sliding shield to vary the O_3 concentration. The gas flow through the cell, usually 5–7 l./min, enters near one end of the cell and exits at the opposite end. It has been established experimentally that there is no appreciable gradient of ozone concentration in the cell. Teflon tubing of ¼-in. o.d. was used for all connections.

To facilitate rapid data acquisition during the comparisons with the GPT method, a Dasibi Model 1003-AH was calibrated against the UV photometer, thus serving as a secondary or "transfer standard". The following procedure was used for calibration of the Dasibi meter. A "span factor" of 56.6 was placed in the instrument, because this value gives approximate agreement with the absolute photometer under the temperature and pressure conditions of our laboratory ($T = 23 \pm 2$ °C, $P = 0.96$ atm) (730 torr). The Dasibi instrument was connected to the photometer at midlength of the absorption cell. With carrier gas flowing, photomultiplier output voltages were read periodically during the calibration procedure and were plotted as a function of time. At intervals, I_t, readings were taken at ozone concentrations in the range 0.05–0.85 ppm of O_3, and the time of the readings was recorded. Simultaneously, readings were taken with the Dasibi meter. For calculation of the ratio I_o/I_t, the appropriate values of I_o were taken from the graph of I_o vs. time. This procedure accounted for the drift in I_o, which was small (about 0.5% per hour) but not negligible. Dark current readings were measured but were negligible with the solar-blind photomultiplier tube and light intensity used in this work. During the calibration, the atmospheric pressure and room temperature were recorded.

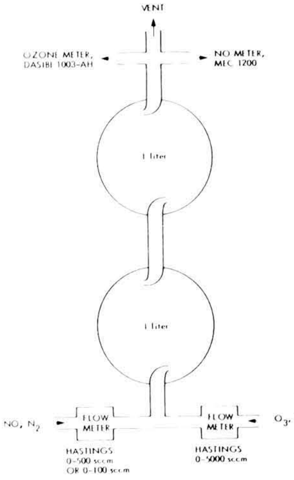

Figure 2. Schematic diagram of gas-phase titration apparatus

The relationship between the photometer readings and the Dasibi readings was then expressed as a linear least-squares equation:

$$O_3(\text{phot}) = (0.999 \pm 0.003)O_3(\text{Dasibi}) - (0.007 \pm 0.002)$$

where the uncertainties refer to 95% confidence limits. These small error limits are indicative of the high precision of the readings taken from both instruments.

To use the above equation at a different ambient pressure, the span factor would be changed in inverse proportion to the pressure relative to the calibration pressure. In practice, such corrections were unnecessary because pressure fluctuations were less than 1%. Temperature corrections to the span factor were also not required since temperature changes in the laboratory were less than ±2 °C.

GPT Apparatus and Methods. A schematic diagram of the GPT apparatus is shown in Figure 2. The NO/N_2 mixture was obtained from a Union Carbide cylinder having a nominal concentration of 52.3 ppm NO. Calibration of this mixture relative to a standard NBS cylinder (45.9 ppm, ±1.1% estimated upper limit of error, 95% confidence limit) indicated a true concentration of 54.3 ppm, and the latter figure was used in the calculations. The O_3/air flow was obtained from the source described above. Both flows were measured with mass flow meters (Hastings-Teledyne), which were calibrated for N_2 and air immediately prior to each daily use by means of bubble meters. The mixing and reaction vessels consisted of two 1-l. bulbs placed in series. The effluent gas was sampled for O_3 with the calibrated Dasibi instrument, and the NO was monitored with an MEC Model 1200 chemiluminescent NO meter. The response of the NO detector was slightly nonlinear in the range of interest, 0.5–2.5 ppm NO. Therefore, the response was calibrated each day by preparation of known NO concentrations based on flow measurements.

The quantities measured in the GPT experiments were the changes in O_3 and NO concentrations, ΔO_3 and ΔNO. Based on unit stoichiometry for the reaction

$$O_3 + NO \rightarrow NO_2 + O_2$$

the relations are

$$\Delta O_3 = \Delta NO$$

$$(O_3{}^i - O_3{}^f) = (NO^i - NO^f)$$

where $O_3{}^i$ and $O_3{}^f$ are the initial and final O_3 concentrations, and similar definitions hold for NO. In practice, excess NO was used, so that the residual O_3 concentrations were small, but not always negligible. The presence of excess NO also precludes possible error due to secondary reaction of O_3 with NO_2, because the rate constant for the O_3 + NO reaction is about 500 times greater than that of the O_3 + NO_2 reaction at room temperature (*14*).

The quantity $O_3{}^i$ was obtained from the following expression:

$$O_3{}^i = \frac{F_{\text{air}}}{F_{\text{air}} + F_{\text{NO}}} \times (O_3{}^i)_{\text{meas}}$$

The quantities F_{air} and F_{NO} are the respective flow rates of the O_3/air and NO/N_2 mixtures, and $(O_3{}^i)_{\text{meas}}$ is the O_3 concentration as measured with the NO/N_2 flow turned off. Since $O_3{}^f$ was measured with both flows on,

$$O_3{}^f = (O_3{}^f)_{\text{meas}}$$

Both NO^i and NO^f were obtained from the calibration data of detector output vs. NO concentration. For purposes of calibration, the NO concentrations were obtained from the equation

$$NO = \frac{F_{\text{NO}}}{F_{\text{air}} + F_{\text{NO}}} \times NO^{\text{cylind}}$$

where NO^{cylind} is the concentration of NO in the standard cylinder.

The O_3/air flow rates were in the range 4–5 l./min, and the NO/N_2 flow rates were in the range 50–250 cc/min, thus giving NO concentrations of about 0.5–2.5 ppm. The O_3 concentrations were in the range 0.3–0.95 ppm.

Results and Discussion

The data, shown in Table II, show good agreement with the predicted relation, $\Delta NO = \Delta O_3$. A linear least-squares treatment gives

$$\Delta O_3 = (1.00 \pm 0.05)\Delta NO - (0.00 \pm 0.01)$$

This result shows that O_3 determination by UV photometry is in good agreement with results obtained by the GPT method, which is traceable to the standard NO/N_2 mixture prepared by the Bureau of Standards. Similar conclusions were recently reported by Hodgeson (*7*) and by Paur (*8*).

It may therefore be concluded that the three candidate methods for O_3 measurement, UV photometry, IR photometry, and GPT, are in substantial agreement, since previous comparisons (*5, 6*) have demonstrated equivalence of the UV and IR methods. All three methods are in poor agreement with the neutral-buffered KI procedure (*5, 6*), indicating that the latter method is not suitable for calibration of ozone monitors.

The question arises as to which methods may be recommended as replacements for the iodometric method. The simplest and most accurate method is to use a Dasibi instrument which has been calibrated against an ultraviolet photometer by a procedure such as that described in the present work. This method was recommended by the CARB Oxidant Calibration Committee and has been in use in California since June 1, 1975.

The IR photometric method requires relatively complex and expensive apparatus and therefore will probably not find extensive use as a laboratory standard for ozone measurement.

Table II. Summary of Results

	NO, ppm		O_3, ppm			
Series[a]	Initial	Final	Initial	Final	ΔNO, ppm	ΔO_3, ppm
a	2.025	1.505	0.519	0.005	0.520	0.514
a	2.010	1.400	0.599	0.005	0.610	0.594
a	2.015	1.245	0.762	0.009	0.770	0.753
b	2.240	1.625	0.602	0.001	0.615	0.601
b	2.365	1.755	0.610	0.005	0.610	0.605
b	2.080	1.330	0.767	0.009	0.750	0.758
c	1.115	0.815	0.311	0.009	0.300	0.302
c	1.130	0.575	0.600	0.032	0.555	0.568
c	1.130	0.425	0.781	0.057	0.705	0.724
c	1.130	0.440	0.738	0.050	0.690	0.688
c	1.130	0.750	0.394	0.010	0.380	0.384
d	2.270	1.545	0.738	0.005	0.725	0.733
d	2.270	1.325	0.950	0.005	0.945	0.945
d	2.270	1.900	0.374	0.003	0.370	0.371

[a] Each series represents data taken during one day.

Our experience indicates that the GPT method is accurate in principle, but that in practice, excessive care must be exercised to obtain accurate results. The susceptibility of this method to error is shown by the fact that it has in the past been reported (*3*) to agree well with the neutral-buffered KI procedure, which is now known to be incorrect. Further, the GPT method showed an error of 9% in tests conducted by the CARB Oxidant Calibration Committee (*5*). The reasons for these previous erroneous results are not known but may be associated with difficulties in the measurement of flow rates. In any case, the method is not sufficiently reliable for routine use as a calibration standard.

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Petroleum Analysis: Methodology for Quantitative and Qualitative Assessment of Oil Spill

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■ An integrated chromatographic technique for petroleum analysis compatible with long-term studies of oil spills is presented. Dynamic headspace sampling and the complementary analytical techniques of gas chromatography and coupled-column liquid chromatography are utilized for quantitation of petroleum containing samples. Gas chromatography–mass spectrometry is employed for identification of individual components in these samples. Analytical data obtained from a major oil spill are presented and discussed.

In the year 1970 alone, approximately 500 000 metric tons of oil were catastrophically spilled in the waterways of the world (*1*). The effects of such spills on the marine environment are of current great concern due to the biological and economic losses which could be sustained. To properly understand the biological damage caused by an oil spill, it is necessary to know the magnitude and composition of the petroleum in water, tissue, and sediment samples collected in the spill area. Furthermore, the analytical methodology developed for this purpose must be compatible with long-term studies in which low levels, as well as the initial high levels, of hydrocarbon pollution are encountered.

This paper details an integrated chromatographic technique (developed as a result of receiving samples from a major oil spill) utilizing dynamic headspace sampling which meets the above criterion. Dynamic headspace sampling is the use of a flowing stream of inert gas to purge a sample of volatile organic components and sweep these components onto an appropriate adsorbent. Through the advent of efficient adsorbents, this technique is receiving considerable current interest for environmental and biomedical trace analysis (*2*). Gas chromatography (GC) and coupled-column liquid chromatography (LC) using a novel internal and external standard technique are employed for quantitation of petroleum containing samples. Gas chromatography–mass spectrometry (GC–MS) is employed for identification of individual components. The two quantitative techniques are uniquely complementary in that they utilize different molecular weight regions and compound classes (aliphatic vs. aromatic hydrocarbons) to arrive at a quantitative answer. Furthermore, an indication of the degree of weathering that has occurred in various samples may be determined by examining the *n*-pentadecane/*n*-undecane gas chromatographic peak height ratios.

Experimental

Samples from the site of a catastrophic oil spill (>50 000 tons of a light Saudi Arabian crude spread along ~100 miles of shoreline) were collected and frozen in the field. Portions of these samples along with a sample of oil taken directly from the tanker after the spill (unweathered spill oil) were shipped to NBS for corroborative analyses. These samples consisted of an oil–water emulsion (M-1), two sediments (S-1 and S-2), a control sediment (S-3) collected beyond the spill area, and a homogenized mussel tissue (T-1). In the laboratory these samples were thawed and transferred under clean conditions to separate headspace sampling flasks containing hydrocarbon-free water.

Quantitation was facilitated by adding known amounts of a solution of internal standards to the weighed quantities of each sample (1 mg to 100 g depending upon the oil content of the sample). The internal standard consisted of a pentane solution of naphthalene and phenanthrene each present at a known concentration (approximately 2 μg per μl). One port of each flask was connected to a prepurified nitrogen line which directs a stream of gas across the liquid interface at a flow rate of ~180 ml/min. A second port contained the exit line, which is connected to a 6 × 0.6 cm stainless steel Swagelok-fitted column packed with Tenax–GC (Applied Science Laboratories, Inc., State College, Pa.) used for trapping the purged organics. This column was mounted in a cylindrical jacket which was chilled by a steady stream of cold air. Samples were purged for 4 h, first at room temperature, and then while gradually raising the temperature to 70 °C. At the end of this period, the nitrogen gas was diverted from the flasks directly to the Tenax columns for 2 h to dry the columns. The dried columns were capped and taken to the instrument laboratory for analysis. Following headspace sampling, the less volatile components were removed by pumping the liquid remaining in the flasks through a liquid chromatographic precolumn packed with Bondapak C18 (Waters Associates, Inc., Milford, Mass.).

The Tenax–GC column from headspace sampling was installed as a precolumn to the analytical column in the gas chromatograph (GC). A heating block was clamped around the precolumn and heated to 375 °C with carrier gas flowing. Just prior to and during this flashing operation, a stream of liquid nitrogen was directed at the head of the analytical column, thus thermally focusing the sample on the GC column. The oven was temperature programmed, and data were acquired. GC–MS data were acquired in an analogous fashion with mass spectra being recorded every 4 s during the course of the entire chromatogram.

The Bondapak C18 columns were coupled to an analytical column packed with μBondapak C18 (microparticulate bonded phase LC packing material) column, and the organic constituents were elution-focused onto the head of the latter using a water–acetonitrile gradient. The gradient was programmed to increase the percentage of acetonitrile in the mobile phase. The effluent from the analytical column was passed through a UV-photometer (254 nm), and the chromatogram was recorded. Details of these headspace sampling and chromatographic procedures are presented elsewhere (*3, 4*).

Additional analyses were performed by Soxhlet extraction to obtain quantitative comparison values. Portions of each sample were Soxhlet extracted for a minimum of 6 h using diethyl ether. The residue remaining in the thimble was weighed to give a total ether-extractable value. Methanol extracts of separate portions of the samples were used for Karl Fischer titrations to determine the percentage of water.

Treatment of Data

Quantitation of Petroleum by GC and LC. Gas chromatograms were quantitated by summing the peak heights of the four aliphatic peaks, *n*-pentadecane to *n*-octadecane (Figure 1) and dividing this sum by the product of the peak height of the naphthalene internal standard and the sample weight used. The value so obtained was then divided by the corresponding value from the unweathered spill oil sample. Upon multiplying by 100, the weight percent oil (wet weight basis) in the sample was obtained (Equation 1).

$$\frac{\left(\sum_{n=15}^{18} h_n\right) \cdot Wc \cdot hc_{\mathrm{NAP}}}{\left(\sum_{n=15}^{18} hc_n\right) \cdot W \cdot h_{\mathrm{NAP}}} \cdot 100 = \text{wt \% oil in sample} \quad (1)$$

where

h_n = peak height of normal aliphatic hydrocarbon of carbon number n in sample chromatogram

hc_n = corresponding peak height from unweathered spill oil sample chromatogram

h_{NAP} = peak height of naphthalene from internal standard in sample chromatogram

hc_{NAP} = corresponding naphthalene peak height in unweathered spill oil sample chromatogram

W = weight of sample analyzed

Wc = weight of unweathered spill oil sample used as external standard

An essentially analogous method was used for liquid chromatographic quantitation. The sum of the peak heights of the three aromatic hydrocarbon peaks (numbered in Figure 2) characteristic of the previously headspace-sampled unweathered spill oil was referenced to the internal standard phenanthrene (Equation 2). Since both the unweathered spill oil and the sample were previously headspace-sampled, any loss of phenanthrene does not affect LC quantitation.

$$\frac{\left(\sum_{p=1}^{3} h_p\right) \cdot Wc \cdot hc_{\mathrm{PHEN}}}{\left(\sum_{p=1}^{3} hc_p\right) \cdot W \cdot h_{\mathrm{PHEN}}} \cdot 100 = \text{wt \% oil in sample} \quad (2)$$

where

h_p = peak height of aromatic hydrocarbon of peak number p in sample chromatogram

Table I. Hydrocarbon Content of Samples Obtained from Catastrophic Oil Spill

		Percent hydrocarbons by various methods[a]				
Sample	**Type**	**Soxhlet extraction corrected for water content (Karl Fischer), %**	**GC, %**	**Coupled-column LC, %**	**Weathering factor (ratio of n-C_{15}/n-C_{11} peak heights)**	**Percent water by Karl Fischer**
M-1	Oil–water emulsion	67 (*1*)[b]	50 ± 20 (*4*)[b]	80 ± 12 (*3*)[b]	7 ± 7	25
S-1	Sediment	0.2 (*1*)	0.2 ± 0.06 (*3*)	0.7 ± 0.07 (*2*)	60 ± 20	0.8
S-2	Sediment	16 (*1*)	9 ± 3 (*3*)	10 ± 1 (*2*)	30 ± 10	16
S-3	Control sediment	Trace (*1*)	0.0002 ± 0.00004 (*3*)	<0.0002 (*2*)	NA	5
T-1	Tissue	7.7 (*1*)	0.03 ± 0.01 (*3*)	1.8 ± 0.2 (*2*)	NA	76
Unweathered spill oil		. . .	. . .	. . .	0.8 ± 0.2	0.2

[a] See text for discussion of methods used. [b] Value in parentheses indicates number of separate determinations.

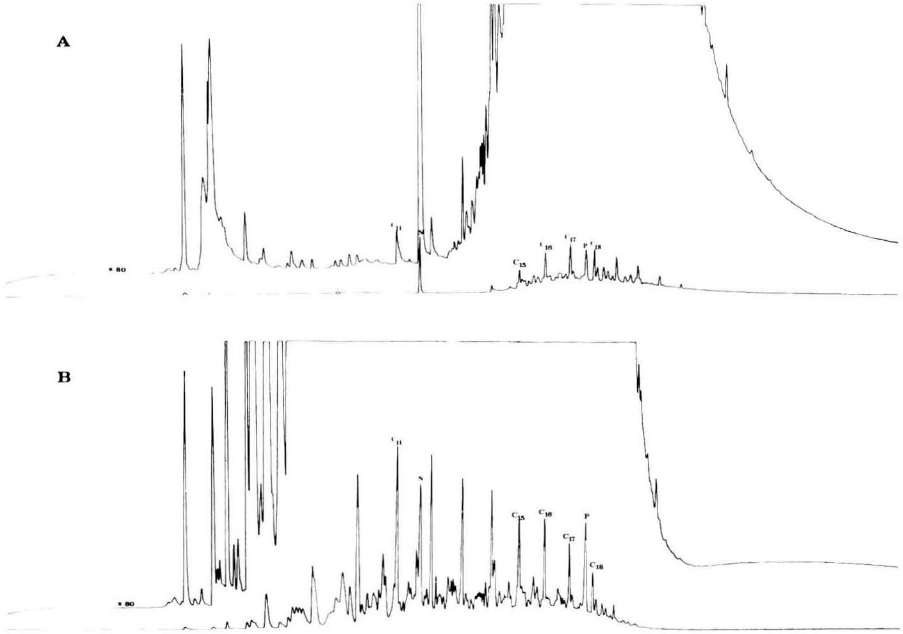

Figure 1. Gas chromatograms from headspace analysis

(A) Sediment sample S-1, (B) unweathered spill oil. Peaks labeled N and P are internal standard compounds naphthalene and phenanthrene, respectively. C_{11}, C_{15}, C_{16}, C_{17}, and C_{18} are *n*-undecane, *n*-pentadecane, *n*-hexadecane, *n*-heptadecane, and *n*-octadecane, respectively. In both (A) and (B), upper trace is 80 times more sensitive than lower trace

hc_p = corresponding peak height from unweathered spill oil sample chromatogram
h_{PHEN} = peak height of phenanthrene from internal standard in sample chromatogram
hc_{PHEN} = corresponding phenanthrene peak height in unweathered spill oil sample chromatogram
W = weight of sample analyzed
Wc = weight of unweathered spill oil sample used as external standard

Quantitation of Petroleum by Soxhlet Extraction and Karl Fischer Titration. The results from the Karl Fischer titrations were used to correct the total ether-extractable values from Soxhlet extraction to total organic content (Equation 3).

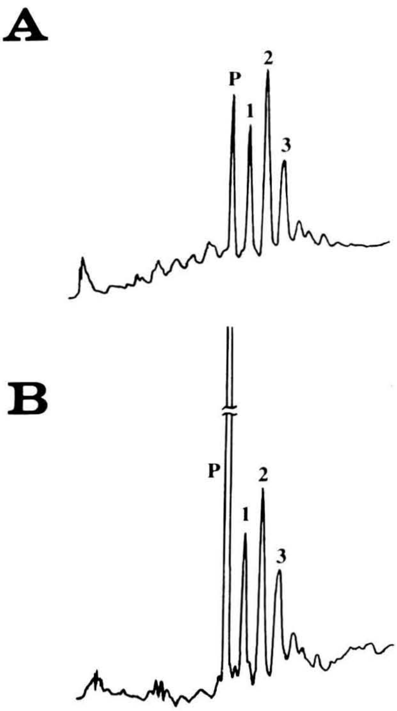

Figure 2. Liquid chromatograms from coupled-column liquid chromatography following headspace sampling

(A) Sediment sample S-1, (B) unweathered spill oil. Peak labeled P is internal standard phenanthrene. 1, 2, and 3 are aromatic hydrocarbons used for quantitation

$$\left[100 - \left(\frac{W_{\mathrm{dry}}}{W} \cdot 100\right)\right] - \%\ \mathrm{H_2O}$$
$$= \text{wt \% extractable organic content of sample} \qquad (3)$$

where

W_{dry} = weight of residue in Soxhlet thimble
W = sample weight
$\%\ \mathrm{H_2O}$ = % water by weight from Karl Fischer titration

The Karl Fischer data were also used to put the gas and liquid chromatographic results on a dry weight basis.

Results and Discussion

Table I contains data obtained on sediment, tissue, and oil–water emulsion samples collected 6 months following the catastrophic oil spill. Figure 1 shows representative gas chromatograms of the headspace-sampled sediment S-1 and the unweathered spill oil. Figure 2 presents the corresponding liquid chromatograms. A total ion chromatogram of the unweathered spill oil is presented in Figure 3. All lettered peaks were identified mass spectrometrically, and the identifications are listed in Table II. As can be seen from Table II, the major components in the chromatogram of the unweathered spill oil can be determined. This information is valuable in determining the source and chemical and biological consequences of the spill oil examined. Of special interest in this particular petroleum was the sulfur content as witnessed by the presence of the dibenzothiophenes.

The combined chromatographic methods presented here are simple to implement in almost any moderately well-equipped laboratory. They involve a minimum of sample handling and avoid the numerous organic extractions of conventional techniques. Since the only solvent necessary is organic-free water, the chances of contamination by impurities in organic solvents are eliminated. These two techniques are uniquely complementary, since they utilize a single sample. Furthermore, the headspace technique can function as a clean-up procedure for the liquid chromatographic technique by removing volatile interferences. The method as presented will accommodate sample sizes from 1 mg to 1 kg. It is applicable to petroleum concentrations as low as 1 mg/kg (ppm) yielding a dynamic range of 10^6. Trace methods using the same experimental apparatus as described above have been developed in this laboratory (*4*) to extend the sensitivity of the analyses to $<\mu$g/kg levels.

In selecting elution peaks for the purpose of quantitation in both the gas and liquid chromatographic procedures, three criteria were of prime importance:

- The peaks must be easily identified within the chromatogram. Mass spectrometry may be invaluable in this regard.
- These peaks must represent compounds for which the method has high sensitivity.

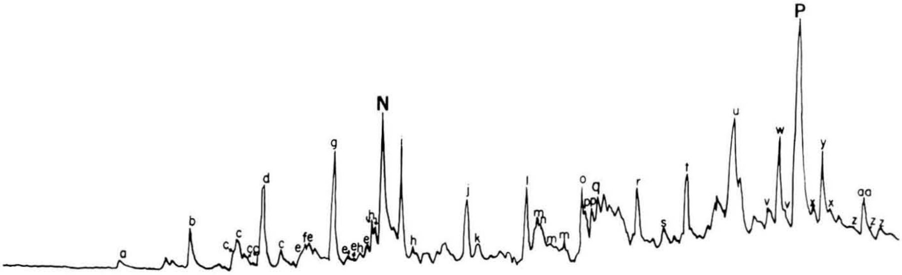

Figure 3. Total ion chromatogram of unweathered spill oil (see Table II for identifications)

Table II. GC–MS Analysis of Unweathered Spill Oil[a]

a = n-C_8
b = n-C_9
c = C_3-benzene
d = n-C_{10}
e = C_4-benzene
f = C_{11} (not n)
g = n-C_{11}
h = C_5-benzene
i = n-C_{12}
j = n-C_{13}
k = C_1-naphthalene
l = n-C_{14}
m = C_2-naphthalene
n = C_6-benzene ?
o = n-C_{15}
p = C_7-benzene ?
q = C_3-naphthalene
r = n-C_{16}
s = C_4-naphthalene
t = n-C_{17}
u = n-C_{18}
v = C_1-dibenzothiophene ?
w = n-C_{19}
x = C_6-naphthalene/C_2-dibenzothiophene
y = n-C_{20}
z = C_7-naphthalene/C_3-dibenzothiophene
aa = n-C_{21}

[a] Computer-generated total ion chromatogram (Figure 3). Peaks labeled N and P are internal standards naphthalene and phenanthrene, respectively. Identifications followed by "?" are not definite due to incompletely resolved spectra. C_x = saturated alkane containing x carbon atoms; C_x-benzene, C_x-naphthalene, C_x-dibenzothiophene = benzene, naphthalene, or dibenzothiophene systems containing substituents totaling x carbon atoms.

- These peaks must represent compounds which are not unduly affected by weathering or other compound specific losses, e.g., absorption, photodegradation.

The aliphatic compounds, n-pentadecane to n-octadecane, utilized for quantitation of the gas chromatographic results met these criteria, being readily identified (Figure 1), optimum for headspace sampling and only minimally affected by weathering. The peaks used in the liquid chromatographic analyses also met these criteria.

LC and GC quantitation were facilitated by use of an internal and external standard procedure. The internal standard (naphthalene for GC, phenanthrene for LC) was added to both the unweathered spill oil and the several samples allowing one to correct for differing recoveries during headspace sampling. Then using the heights of a few selected peaks appearing in the chromatograms of both the samples and the reference unweathered spill oil, one could directly quantitate the oil levels in the various samples.

Karl Fischer titrations were necessary to be able to express oil concentrations in sediments and tissue samples on a dry weight basis. Soxhlet extractions were used only as a confirmatory method and, as discussed below, lead to erroneously high values when biogenic extractable organic compounds are present.

Weathering, as defined as the loss of the lower molecular weight petroleum compounds from the sample, is indicated by the ratio n-pentadecane/n-undecane (Figure 1 and Table I). The base compound, n-pentadecane, was selected for much the same reasons as recently outlined by Harrison et al. (5); it appeared to show little weathering losses in the various gas chromatograms. The individual weathering numbers (Table I) in themselves have no absolute meaning, but in a relative sense, provide some insight into the degree of weathering that has occurred.

The generally high standard deviations of the results (standard deviations of the means) in Table I can be explained in terms of sample inhomogeneity and the limited amounts of the samples available for analysis. When small samples were dictated (by their high petroleum content), they were by nature inhomogeneous and not representative of the whole. When large samples were dictated (due to the low levels, <0.1%, of petroleum present), the rather small amounts of sample supplied precluded the running of sufficient replicates. Sample M-1 was a particular problem since it was an oil–water emulsion which was impossible to subsample reproducibly for replicate analyses.

The marine tissue sample, T-1, when analyzed by Soxhlet extraction, gas chromatography, and liquid chromatography gave widely divergent values for oil content. Since tissue has a large amount of biogenic extractable compounds of nonpetroleum origin, high values are to be expected by Soxhlet extraction. Work in this laboratory indicates that marine bivalves (oysters) concentrate aromatic compounds in their tissues when exposed to petroleum. The liquid chromatographic method is much more sensitive to aromatic compounds because it utilizes an ultraviolet detector (254 nm). Thus tissue from organisms exposed to petroleum and analyzed by this method could be expected to also yield somewhat high values for oil content. The gas chromatographic results may be somewhat low, since marine organisms can depurate aliphatic compounds. The true result probably lies somewhere between the gas and liquid chromatographic values.

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Atmospheric Particulate Mass Measurement with Beta Attenuation Mass Monitor

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■ A two-stage on-line mass monitor with aerosol size separator (TWOMASS) employing the beta attenuation technique has been developed for monitoring of atmospheric aerosols with high time resolution. This instrument independently analyzes the mass concentration of two particle size fractions. Coarse particles are inertially separated by impaction on filter paper. The fine particle fraction is collected on a high-efficiency glass-fiber filter. Carbon-14 is used as a source of beta particles which are detected by a silicon surface-barrier detector coupled to fast, low-noise nuclear electronics. A programmable calculator controls TWOMASS, calculates the mass concentration of each size fraction, plots, prints, and stores the data on tape. The instrument has been gravimetrically calibrated using laboratory and atmospheric aerosols. For 10-min sampling intervals, the precision of the instrument is 4 $\mu g/m^3$, and the accuracy is 11%. It has subsequently been field tested by sampling atmospheric aerosol over an extended period which indicates that it is capable of ambient air monitoring with a time response on the order of 10 min.

The present air quality standard for particulate matter is expressed in terms of the total aerosol mass concentration in $\mu g/m^3$ as measured by the high-volume air filter sampler. Recently, there has been concern among researchers, as well as within control agencies, that total particulate mass or any other single parameter is an inadequate and, to some extent, misleading measure of adverse effects of atmospheric particles. There is an increasing body of evidence which suggests that atmospheric particles of diameters less than 5 μm contribute significantly to the adverse effects of air pollution and in fact constitute a large segment of the total air pollution problem (*1*). Accordingly, the current thinking on a first step toward a proper characterization of atmospheric particles is to divide the total aerosol population into two size classes, i.e., *fine* and *coarse* particles (*2*). A study of the characteristics of the Los Angeles smog aerosol by Whitby et al. (*3*) and subsequent studies of other locations by Durham et al. (*4*) showed that most of the atmospheric aerosol volume is distributed bimodally, as shown in Figure 1. The lower mass mode is in the size range 0.1–1.0 μm, while the upper mode is over 5 μm. The minimum between the two mass (or volume) modes is between 0.8 and 3.0 μm. The bimodal aerosol mass spectrum is significant because the two modes have distinctly different elemental composition, as shown by Dzubay and Stevens (*5*) and physical characteristics (*6*) (particle shape, volatility). Furthermore, the two modes are produced by different sources (*7, 8*), and they are associated with different effects. These findings provide a scientific rationale for the separate consideration of fine and coarse particles.

It is anticipated that within the next few years, these findings may be recognized by establishing new standards requiring the determination of aerosol mass and composition as a function of particle size. Independent determination of the mass concentration of only two size fractions will probably be adequate for monitoring purposes (*2*). The division of lower and upper mass modes will depend on two major criteria. First, the separation should reflect the bimodality of the atmospheric aerosol size spectrum. Secondly, the separation should take into account the ability of different size particles to affect human health, visibility, weather and climate, etc. (Figure 1).

The attenuation of beta particles as they pass through an absorber can be used as a thickness gauge or mass monitor. In earlier studies, various source and detector combinations were used (*9–13*). An application of the beta absorption technique for determining the mass concentration of atmospheric particles was reported by Nader and Allen in 1960 (*14*). That work demonstrated the feasibility of this technique for use in automated tape samples. More recently, many researchers have reported the use of beta attenuation mass monitors using a variety of experimental configurations (*15–25*). In a recent comprehensive study of potential techniques for measurements of emissions from fossil fuel combustion sources, Sem et al. (*26*) identified beta attenuation as a promising method for sensing particle mass concentration. A detailed review of the application of this method for mass measurement is given elsewhere (*27*).

This paper is concerned with application of the beta attenuation technique for automated atmospheric particle mass measurements. A two stage on-line mass monitor with aerosol size separator (TWOMASS) which monitors atmospheric aerosols in two size ranges is described. The operating characteristics, calibration of the instrument, and field tests are discussed.

Physics of Beta Absorption

In the process of β^- decay, an electron is emitted from the atomic nucleus, and the nuclear charge changes from Z to $Z + 1$ in units of the electronic charge. This process transmutes the beta-active element into the next heavier element. Beta particles are emitted with a continuous energy spectrum rather than a single discrete energy equal to the transition energy. For ^{14}C, the beta source used in this work, the decay can be depicted as follows:

$$^{14}C \rightarrow {}^{14}N + \beta^- + \bar{\nu} \tag{1}$$

The average beta particle energy is approximately one-third of the maximum energy for most beta emitters.

Beta particles interact with matter through elastic and inelastic scattering with atomic electrons and through elastic scattering with nuclei. For low-energy electrons ($E_\beta < 0.5$ MeV), inelastic scattering with atomic electrons (ionization) is the predominant mode of energy loss (*28*). The number of beta particles passing through an absorber decreases exponentially with absorber thickness, to a good approximation, as given by the following (*29*)

$$I = I_o e^{-\mu_m x} \tag{2}$$

where I_o is the beta intensity without an absorber, I is the intensity observed through an absorber of thickness x, and μ_m is the mass absorption coefficient. The exponential form of the curve is fortuitous, since it also includes the effects of

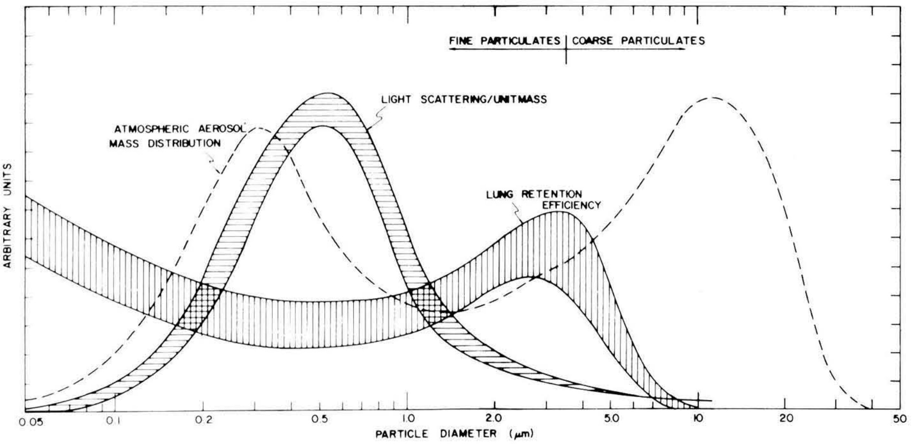

Figure 1. Distribution of atmospheric aerosol mass, light scattering/unit mass, and lung retention efficiency plotted with respect to particle diameter

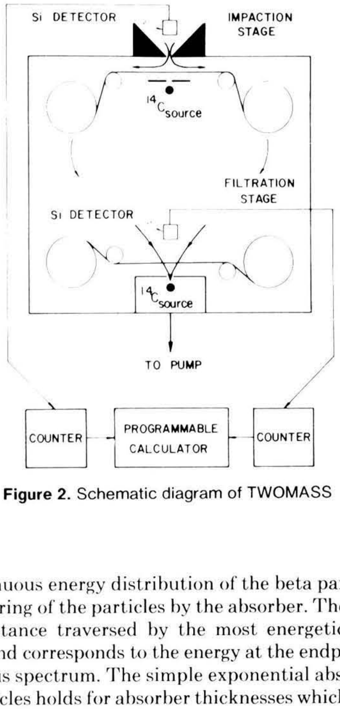

Figure 2. Schematic diagram of TWOMASS

the continuous energy distribution of the beta particles and the scattering of the particles by the absorber. The range, R, is the distance traversed by the most energetic particles emitted and corresponds to the energy at the endpoint of the continuous spectrum. The simple exponential absorption of beta particles holds for absorber thicknesses which are small compared to the beta particle range (*29*).

For low-energy beta emitters, the mass absorption coefficient is nearly independent of the chemical composition of the absorber. The absorption of high-energy radiation ($E_\beta > 1$ MeV) includes a bremsstrahlung radiation component (inelastic scattering with the nuclear coulomb field). This effect causes large variations in the mass absorption coefficient with increasing atomic number (*30*) and is largest for heavy element absorbers.

Instrument Design

The TWOMASS instrument was designed to separate particles into two size classes and to measure aerosol mass concentration with high time resolution. Many of the details of optimal design criteria are given in a recent review (*27*).

Aerosol Collection System. The flow system separates particles into two size fractions. Coarse particles are impacted on a glass fiber filter; the remaining particles are collected on an identical high-efficiency glass fiber filter. This system is shown schematically in Figure 2. The single-stage impactor head has a 4.5-mm diam inlet aperture with a 4.5-mm jet-to-plate distance. The impactor was designed to have 50% efficiency for particles of 3.5 μm diam. This cutoff size was chosen as a compromise between the proper separation of the two modes of the atmospheric aerosol and the simulation of the aerosol removal characteristics of the human upper respiratory system.

Various impaction materials were tested, and a Pallflex (Pallflex Products Corp., Putnam, Conn.) glass fiber filter with thin cellulose backing was the most satisfactory because of its low mass density, efficient impaction properties, and uniform thickness. Lilienfeld and Dulchinos (*19*) found that this filter has high particle collection efficiency at high face velocities, low flow resistance, low tare weight, adequate mechanical strength, and adequate filter capacity before clogging. The mass density of this filter is 3.2 mg/cm^2, and the efficiency is over 99% for both cigarette smoke and 0.3 μm diam. polystyrene latex spheres (*19*). This filter was used for both stages of the sampler. The flow rate through the TWOMASS was set at 400 cm^3/s (24 l./min). The face velocity under operating conditions was 13 m/s.

Source and Detection System. Both the impaction and filtration heads of TWOMASS have independent source-detector systems. The beta source chosen was 3 mCi of ^{14}C deposited as sodium acetate in a 6-mm diameter copper disk covered with 800 μg/cm^2 of mylar film. This source is a pure low-energy beta emitter with 5.7×10^3 year half life, E_{max} = 156 keV, and range R = 28.3 mg/cm^2 (*31*). The total density of all absorbers (air, detector window, filters, deposited mass, etc.) in the system is about 6 mg/cm^2 or about 21% of the range of ^{14}C beta particles, which is optimal for measurement sensitivity (*11*). The cross-sectional areas of the collection spots in the filtration and impaction states are 32 and 16 mm^2, respectively.

The beta detector (ORTEC, Inc., Oak Ridge, Tenn.) is a silicon surface-barrier detector with a 50-mm^2 surface area, a 40-μg aluminum window, and a noise width less than 11 keV. This detector is light-tight and rugged, and hence suited for field operation. It was chosen because of its high count-rate capability, low-noise characteristics, low cost, and simplicity of operation. The amplified output of each detector is acquired with two high-speed counters and further processed by a Tektronix programmable calculator with an x-y point plotter, printer, and magnetic tape cassette. The average aerosol mass concentration, ΔM in $\mu g/cm^2$, is given by

$$\Delta M = \frac{A}{Q \Delta t \mu_m} \ln (I_o/I) \qquad (3)$$

where A is the cross-sectional area of the collector, Δt is the counting and collection interval in seconds, Q is the flow rate in cm^3/s, μ_m is the mass attenuation coefficient in units of $cm^2/\mu g$, I is the count rate of the current interval, and I_o is the count rate through the filter before the addition of ΔM.

On-Line Operation. The TWOMASS instrument is operated as a spot sampler with aerosol deposited continuously on both stages. The filter tapes are advanced simultaneously every 2 h to avoid clogging. In operation with atmospheric aerosol, the change in the flow rate is less than 5% during a 2-h interval. The beta particles which penetrate the filter paper are counted as aerosol is being deposited. The values of I and I_o, appearing in Equation 3, are the number of counts accumulated in the current and previous time intervals, respectively. The mass determination is made for each 10-min counting interval. In this way, 11 mass concentrations are acquired during the accumulation of each 2-h filter spot. (No mass measurement can be made during the first time interval.)

Calibration

The instrument was calibrated gravimetrically with laboratory and St. Louis atmospheric aerosols. The results of these measurements yield an exponential relationship between beta attenuation (I/I_o) and gravimetric mass, both for laboratory aerosols in the range of 1–7 mg/cm^2 and for atmospheric aerosols in the range of 0.2–1 mg/cm^2, as shown in Figure 3. The calibration was carried out over a much wider mass range than required for TWOMASS when used for ambient monitoring. In a typical 3-h period of aerosol collection in St. Louis, the deposited particulate mass on either stage is no more than 1 mg/cm^2.

The mass attenuation coefficient, μ_m, depends on the chemical form of the aerosol as shown in Figure 3. These data indicate that μ_m varies from 0.20 for glycine to 0.26 for atmospheric aerosol. Thus, we suggest that the determination of μ_m is necessary when using TWOMASS for studying a specific aerosol. However, our data indicate that, at least for St. Louis, the atmospheric aerosol has a value of μ_m = 0.26 ± 0.03 cm^2/mg. This value, perhaps fortuitously, is identical with the standard literature value of 0.26 cm^2/mg (*31*).

Precision. The total precision of the instrument is a function of the stability of the system and the counting statistics. Typical counting rates are 10 000 cps with the unloaded filter tape in place. The count rate is reduced by 0.4% due to an aerosol mass collected in a 10-min interval. This high counting rate was possible with minimal dead time (<1%) because of the fast timing characteristics of the semiconductor detector and associated electronics. The uncertainty, E, based only on counting statistics using the 2 σ error limit for a given instrumental design, is a function of counting time only (*32*):

$$E_{\min}(2\sigma) = \frac{K_o}{t}$$

For TWOMASS with the conditions described above, this constant is K_o = 2000 $\mu g \cdot s/m^3$. For sampling times of 600 s, the total precision of TWOMASS, including both the statistical uncertainty and the instrumental stability for normal field operations, is 4 $\mu g/m^3$. The system has also been run with subsecond time intervals for laboratory experiments using high aerosol mass concentrations.

Accuracy. The accuracy of the mass concentration measurement as determined in Equation 2 is determined mainly by the uncertainty in the mass attenuation coefficient for the particular aerosol being measured. For St. Louis atmospheric aerosol, the total accuracy is 11% based on a 10% uncertainty in μ_m (Figure 3b), 5% uncertainty in flow rate, and less than 0.1% uncertainty in sample area, time interval, and (I_o/I). However, the accuracy is affected by several other factors. These include losses in the inlet system, filtration and im-

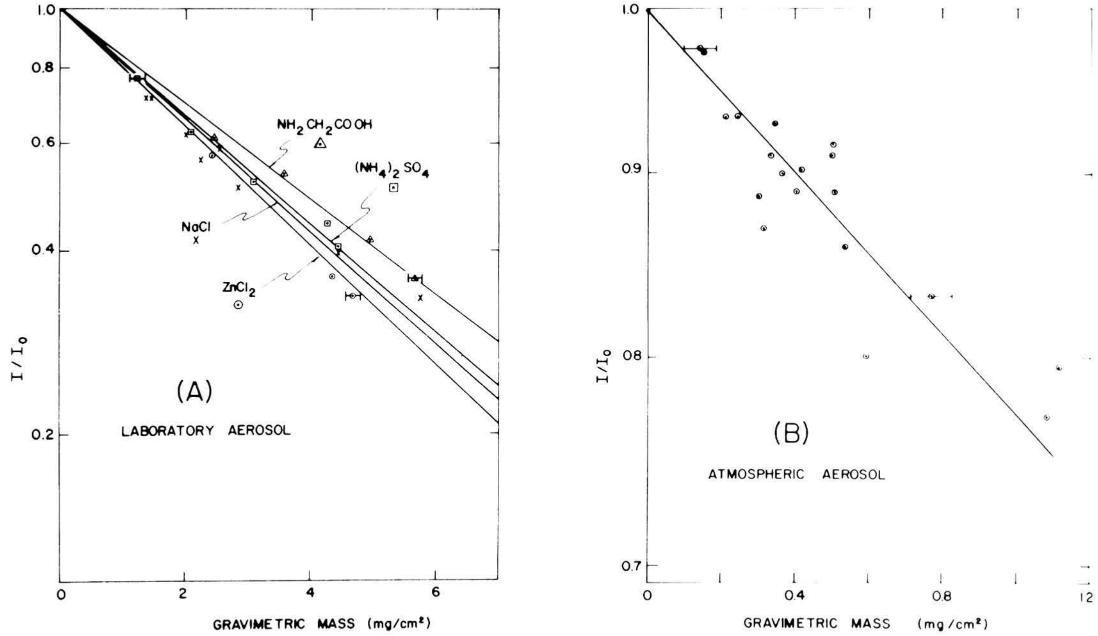

Figure 3. Gravimetric calibration of TWOMASS using a) laboratory aerosols and b) St. Louis atmospheric aerosol

paction efficiency, and sample loss or gain during and after decomposition. At present, the magnitudes of these effects. are being studied in detail.

Field Testing with Atmospheric Aerosols

A study of the ambient aerosol mass concentration using TWOMASS with 10-min sampling intervals and moving the filter tapes every 2 h was carried out in August 1975 at Station 106 of the Regional Air Monitoring System (RAMS) in St. Louis. The particulate sulfur content of both the fine and coarse modes was also determined by analyzing the 2-h sample spots using the flash vaporization–flame photometric detection method (*33*).

In Figure 4 the fine and coarse ambient aerosol mass concentration is plotted for a two-day period. The 2-h average particulate sulfur concentration in each fraction is also shown in Figure 4. These data show that the mass of both the fine and coarse fractions exhibits substantial temporal variation in a time scale of less than 1 h. It is also evident that the mass variation of the two modes is at times decoupled. However, the two modes are correlated with a liner correlation coefficient of 0.7 determined over a two-week period. During this period the mass concentration in each mode varied between 5 and 60 μg/m^3, which is not atypical of mass concentrations measured at other times in St. Louis (*34*).

The data indicate that sulfur constitutes approximately 10% of the fine particle mass, and that there is an unexpectedly small variation of the sulfur to fine particulate mass ratio. If particulate sulfur is in the form of $(NH_4)_2SO_4$, about 41% of the fine particulate mass can be accounted for. Sulfur contributes less than 2% of the coarse particulate mass, and the sulfur fraction is far more variable with time.

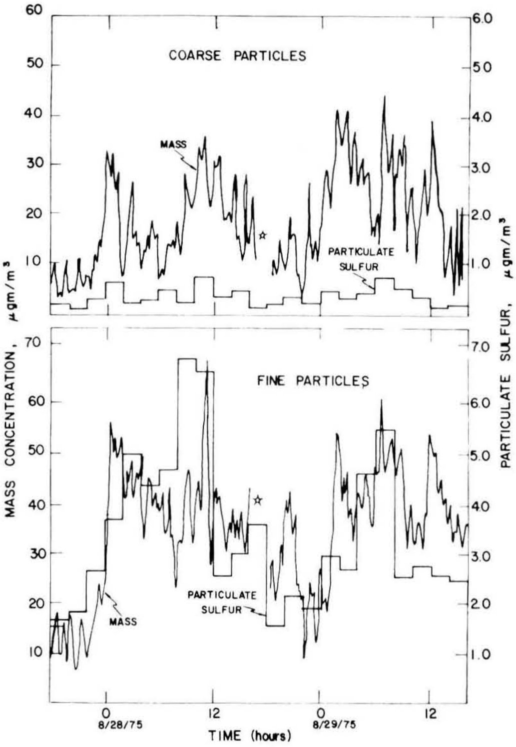

Figure 4. Aerosol mass concentration data for St. Louis atmospheric aerosol during August 1975 and sulfur concentration data determined off-line using flash vaporization–flame photometric detection method. Star in figure indicates time of rainstorm

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Ozone Formation Potential of Organic Compounds

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■ A reactivity scale for organic compounds based on ozone production is developed. It is based on the concept that ozone can be considered as the intermediate (B) of two consecutive reactions, $A \rightarrow B \rightarrow C$. The organic compound, A, is assumed to react only with OH radicals that are present in the atmosphere. It is also assumed that the organic compound is completely oxidized to either CO_2 and/or formic acid. A reactivity scale based on these premises heavily weighs the number of carbon and hydrogen atoms present in the compound. The scale, developed only on theoretical grounds, predicts that all hydrocarbons lead to ozone formation and that the larger molecules lead to larger quantities of ozone. The reactivity scale predicts that high concentrations of ozone would be expected in rural downwind areas away from high emissions sources. This is in agreement with recent findings of high ozone levels in rural areas.

Organic matter including hydrocarbons is essential for the formation of photochemical smog. However, not all hydrocarbons manifest themselves equally in the smog symptoms such as eye irritation, plant damage, visibility reduction, and oxidant formation. The literature suggests that several of these symptoms of reactivity must be considered when planning control strategies (*1–3*). However, for the present, oxidant/ozone is the only photochemical product for which there is an Air Quality Standard. Achievement of the oxidant standard is based on control of organic emissions.

The role of the oxidant precursors, i.e., the hydrocarbons, has been extensively studied in many laboratories over the past several years. Various parameters such as types of hydrocarbons, HC/NO_x ratios, light intensity, water vapor, and temperature have all been investigated for possible effects on oxidant formation (*1*). From these studies, definitions of reactive organics such as those given in Rule 66 (*4*) have been developed by the Los Angeles County. The Rule 66 approach is to limit the emissions of hydrocarbons that are relatively high in reactivity with the expectation that this will result in a decrease in the amount of oxidant produced in the atmosphere of Los Angeles County.

Appendix B in the *Federal Register* (August 1971) tends to overlook the relative reactivities of different hydrocarbons and puts forth the concept that all but a few hydrocarbons should be controlled. This approach severely limits emissions of all but the most unreactive hydrocarbons.

More recently, a linear summation model for the control of hydrocarbons has been proposed (*5*). With this model, hydrocarbons are classified according to five reactivity classes. Any combination of these five classes could be emitted into the atmosphere as long as the linear summation does not exceed the reactivity of the class of least reactive hydrocarbons.

Some recent findings in the Midwest by EPA (*6*), as well as recent investigations (*7, 8*) of high oxidant in rural areas, have led us to look into the formation of high oxidant concentrations from the so-called unreactive hydrocarbons. Smog chamber studies have shown that unreactive or moderately reactive hydrocarbons, i.e., the paraffins, can produce high ozone concentrations when irradiated over a prolonged period (*9*). This is the condition that a hydrocarbon is subjected to when irradiated for several days during transport. These findings led us to believe that a modified Appendix B approach is appropriate, i.e., all hydrocarbon emissions regardless of reactivity must be considered as candidates for control since they all lead to ozone formation.

We have derived a reactivity scale for O_3 formation based on theoretical considerations. The basis of this scale is the differences in rates between O_3-forming reactions and O_3-degradation. No experimental values other than known rate constants are employed.

Assumptions

The basic assumption of the method is that hydrocarbons are degraded principally by their reaction with OH radicals. In the presence of small quantities of oxides of nitrogen, ozone is ultimately formed. The extent to which O_3 is produced will depend upon the rate of production of O_3 as compared to the rate of destruction.

Ozone can be considered as an intermediate, B, of two consecutive reactions

$$A \xrightarrow{k_a} B \xrightarrow{k_b} C$$

where A is the hydrocarbon, and C is the degradation product of ozone, O_2. The rate constants k_a and k_b may be a composite of several rate constants. In the case of a fast reacting hydrocarbon, such as an internally double-bonded olefin, ozone will be observed because $k_a \gg k_b$, i.e., the rate(s) at which O_3 is produced is much greater than the rate(s) at which O_3 reacts. In the case of a slow reacting compound such as methane, the reactions involving degradation are greater than those involving ozone formation ($k_a < k_b$). As a consequence, little ozone is observed in the photooxidation of methane. The internal double-bonded olefins and methane are the two extremes of hydrocarbon reactivity. When a moderately reactive hydrocarbon is considered so that $k_a \simeq k_b$, then some intermediate concentration of ozone can be expected. Construction of the reactivity scale is based upon the theoretical average O_3 that one can expect to be produced during the time interval for 99% of the hydrocarbon to react. Synergistic effects are not relevant in this proposed reactivity scale. The reason for this is that only the maximum oxidant-forming potential of the hydrocarbon is considered. Synergistic effects would not significantly affect this potential. In the construction of this scale, the following premises are used:

- The degradation of the hydrocarbon under consideration is initiated by its reaction with OH. The hydrocarbon is eventually completely degraded to CO_2 and/or formic acid.
- The oxidation of NO to NO_2 by RO_2, RCO_3, and HO_2 radicals, which are formed in the hydrocarbon degradation process, always leads to ozone formation. The photochemical decomposition of NO_2 will produce one molecule of O_3. The radicals RO_2, RCO_3, and HO_2 are never taken as reactants in a chain terminating reaction.
- The OH radical concentration is assumed to be constant, and a value of 1.7×10^{-6} ppm (V/V) was used in the calculations. This is the approximate concentration given by a computer model of the atmospheric oxidation of 1 ppm of CO in the presence of 50 ppb of NO and 10 ppb of NO_2. The concentration of OH radicals is in the same general level as that calculated by others (*10, 11*). The OH concentration is expected to be zero at nighttime hours. This was not considered in the model.
- A unimolecular decay constant for O_3 was derived. This decay constant is a composite rate for all the decay paths for

O_3 except for its reaction with NO, its reaction with olefins, and its deposition reactions. The reaction of O_3 with NO is not a degradation path since NO_2 is formed which will photodecompose and result in reforming the O_3. The reaction of NO with O_3 was also considered with concentration of NO kept at a constant value of 5 ppb (V/V). This will be discussed later. The reaction of O_3 with olefin was not considered because its contribution was minimal. It was found to be most important with a fast reacting olefin like *trans*-2-butene. However, even in this case, its contribution was only 0.3% to the average ozone provided. The depletion of O_3 by dry deposition was not considered since the problem is extremely complex. We do not know, for example, the atmospheric stability or the ground terrain in which the calculations should be made. Also, even if the calculation for a specific diffusion rate were made, the rate would change during the course of the day as the temperature inversion lifts. Therefore, it was decided that this parameter, ground deposition, is important but cannot be included until better meteorological models become available. To obtain the composite decay constants, O_3 degradation was simulated by a computer model. The model chosen was the reactions of 0.2 ppm O_3, 1.4 ppm CH_4, 0.1 ppm CO, at 50% relative humidity, and a 40° solar zenith angle. These concentrations of methane and CO were chosen since they are the geophysical concentration levels of these compounds. The relative humidity and solar zenith angle were arbitrarily chosen. The mechanism involved 31 reactions which include the photodissociation of O_3 by sunlight and the subsequent reaction of $O(^1D)$ with water to produce OH radicals. The OH radicals react with CH_4 and CO that are present. A plot of log (O_3) vs. time gave a straight line from which a unimolecular decay constant of 1.6×10^{-3} min^{-1} was derived. This constant is used in the calculations. As with the change in OH concentration, the decay rate for ozone is expected to be altered during the nighttime hours. This was not considered in the model. Both the OH concentration and the O_3 decay rate could be made time dependent. However, this would add to the complexity of the calculations and would not significantly alter the conclusions.

Existing reactivity scales are based on ozone formation data obtained from smog chamber irradiations. These data are usually obtained by irradiating for several hours a mixture of hydrocarbon, oxides of nitrogen, and water vapor. Generally, the irradiation period is for only 3–6 h, and the maximum O_3 concentration produced is used to construct a reactivity scale. If the reactivity of the organic compound is low, little of the hydrocarbon reacts, and as a result little ozone is produced. In our proposed reactivity scale, the reactivity parameter is the average O_3 produced during the time required for 99% of the hydrocarbon to react. For comparison purposes, the O_3 concentration at the peak O_3 value, (O_3) max, is calculated.

In these calculations, the time required for 99% reaction of the hydrocarbon and the time to the ozone peak value refer to daylight time, time during which the light intensity corresponds to a solar zenith angle of 40°. The OH concentration can be expected to approach zero during the nighttime hours.

Method of Calculation

Maximum Possible Ozone. The maximum possible number of O_3 molecules that can be produced from one hydrocarbon molecule is calculated on the basis of the first two premises. A mechanism is written for the oxidation of the organic compound. The oxidation is initiated by reaction with OH, and the hydrocarbon is completely degraded to CO_2 and/or formic acid. Only those reactions which are thermodynamically possible are considered in the degradation process. The maximum possible number of O_3 molecules that can be produced from one hydrocarbon molecule can then be calculated from the number of times RO_3, RO_2, and HO_2 radicals react with NO to form a NO_2 molecule. To illustrate, using CH_4 as an example,

$$CH_4 + OH \rightarrow CH_3 + H_2O \tag{1}$$

$$CH_3 + O_2 \rightarrow CH_3O_2 \tag{2}$$

$$CH_3O_2 + NO \rightarrow NO_2 + CH_3O \qquad \text{I} \tag{3}$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \tag{4}$$

$$HO_2 + NO \rightarrow HO + NO_2 \qquad \text{II} \tag{5}$$

$$HCHO + OH \rightarrow H_2O + HCO \tag{6}$$

$$HCO + O_2 \rightarrow HO_2 + CO \qquad \text{III} \tag{7}$$

$$CO + OH \rightarrow HO_2 + CO_2 \qquad \text{IV} \tag{8}$$

Reactions 3, 5, 7, and 8 can form a molecule of NO_2, i.e., from one molecule of CH_4, four molecules of NO_2 are formed, and hence four molecules of O_3 will be formed. For each class of organic compounds, a formula can be derived for the maximum number of O_3 molecules that can be formed as shown in Table I. Because the number of ozone molecules produced by OH abstraction and OH addition are not the same with respect to olefin and acetylene, only the abstraction is used in the remainder of the calculation, as a first approximation. Since a thorough product study has not been made for aromatic compounds, a mechanism could not be written for the aromatics without considerable speculation. We assumed that the number of O_3 molecules produced from the aromatics is equal to those produced by olefins with OH abstractions.

There is a question as to the validity of using the values from Table I for the aromatics. These hydrocarbons produce aerosols when photooxidized in the presence of oxides of nitrogen. The carbon balance in these systems is generally poor, and a large quantity of the hydrocarbon fragment is presumed to go to the walls of the reaction vessel (*12, 13*). Therefore, the values shown in Table I for the amount of ozone produced for a unit value of aromatic hydrocarbon are probably not valid since the ultimate decay product is not CO_2 for these hydrocarbons in the atmosphere. A more reasonable fate for the bulk of the aromatics is probably aerosol formation and deposition.

Time for 99% Reaction. To derive the time for 99% of the organic compound to react, a simple second order reaction rate is used:

$$\frac{-d(A)}{dt} = k_a(\mathrm{OH})(A) \tag{9}$$

$$t_{99\%} = \frac{4.6}{k_a(\mathrm{OH})} \tag{10}$$

By use of this expression and assuming that the (OH) concentration is 1.7×10^{-6} ppm, the values in Table II were calculated. The rate constants, k_a, used in the calculation are also given in Table II.

Table I. Maximum Possible Ozone Produced from Various Classes of Organic Compounds

Compound	Max poss ozone[a]
Monoaldehydes	$nC + nH - 1$
Alkanes	$nC + nH - 1$
Monoalkenes (OH abstraction)	$nC + nH$
Monoalkenes (OH addition)	$nC + nH - 1$
Monoalkynes (OH abstraction)	$nC + nH + 1$
Monoalkynes (OH addition)	$nC + nH$
Aromatics	$nC + nH$

[a] nC and nH are the number of carbon atoms and number of hydrogen atoms, respectively, in the specific compound.

Average O_3 Produced During 99% Reaction. The rate of formation of ozone can be expressed as:

$$\frac{1}{n'}\left(\frac{d(O_3)}{dt}\right)_{\text{form}} = \frac{-d(A)}{dt} = k_a[A][\text{OH}] \qquad (11)$$

where n' is the maximum possible number of ozone molecules that can be produced from one molecule of hydrocarbon A (column 2 in Table I). The rate of decay of O_3 is

$$\left(\frac{d(O_3)}{dt}\right)_{\text{decay}} = 1.6 \times 10^{-3}\,(O_3) \qquad (12)$$

Equations 11 and 12 are combined to give the net rate of production of O_3:

$$\frac{d(O_3)}{dt} = nka(A)(\text{OH}) - 1.6 \times 10^{-3}\,(O_3) \qquad (13)$$

The first term of the above can be rewritten as

$$n'k_a(\text{OH})e^{-k_a(\text{OH})t} \text{ since } A = e^{-k(\text{OH})t}$$

The solution to Equation 13 is then

$$O_3 = n'k_a(\text{OH})\frac{e^{-k_a(\text{OH})t} - e^{-1.6\times10^{-3}\,t}}{1.6 \times 10^{-3} - k_a(\text{OH})} \qquad (14)$$

Since the average value of any quantity is given by

$$\langle O_3 \rangle = \frac{1}{t_f - t_i}\int_{t_i}^{t_f} O_3 dt \qquad (15)$$

then

$$\langle O_3 \rangle = \frac{1}{t}\int_0^t n'k_a(\text{OH})\frac{e^{-k_a(\text{OH})t} - e^{-1.6\times10^{-3}\,t}}{1.6 \times 10^{-3} - k_a(\text{OH})}dt \qquad (16)$$

If we substitute t for 99% reaction (Equation 10) and ignore $e^{-k_a(\text{OH})t}$ since this term is small, we obtain

$$O_3 = \frac{n'[k_a(\text{OH})]^2}{4.6[1.6 \times 10^{-3} - k_a(\text{OH})]} \times \left(\frac{1}{k_a(\text{OH})} - \frac{1 - e^{-7.36\times10^{-3}/k_a(\text{OH})}}{1.6 \times 10^{-3}}\right) \qquad (17)$$

By assuming that (OH) = 1.7×10^{-6} ppm and using the rate constants, ka, given in Table II for the HC + OH reactions, Table III was constructed. The time for 99% reaction (column 2, Table II) for the hydrocarbons is probably short for actual atmospheric conditions. The OH concentration is expected to be very low or zero during the nighttime hour.

Table II. Reactivity Parameters for Various Organic Compounds

Compound	Time for 99% reaction, min	Time to peak ozone value, min	(OH) rate constant, $\text{ppm}^{-1}\,\text{min}^{-1}$	Refs for rate constant
1,2,4-Trimethyl benzene	61.6	48.5	4.9×10^4	(*11*)
m-Xylene	87.4	63.9	3.4×10^4	(*11*)
Toluene	492	224.4	1.7×10^4	(*11*)
Benzene	529	225.4	5.6×10^3	(*11*)
trans-2-Butene	25.5	26.7	10.5×10^4	(*14*)
Propene	128.8	91.2	2.1×10^4	(*15*)
Ethene	602.6	259.5	4.5×10^3	(*15*)
Acetylene	1.22×10^4	1178.9	2.2×10^2	(*15*)
n-Butane	768.2	303.4	3.5×10^3	(*15*)
Ethane	6026	886.2	4.5×10^2	(*15*)
Methane	2.25×10^5	2777.1	1.2×10^1	(*15*)
Butyraldehyde	123	88.0	2.2×10^4	(*14*)
Propionaldehyde	123	88.0	2.2×10^4	(*14*)
Acetaldehyde	123	88.0	2.2×10^4	(*14*)
Formaldehyde	128.8	91.2	2.1×10^4	(*15*)
Carbon monoxide	1.28×10^4	1209.7	2.1×10^2	(*15*)

Table III. Ozone Produced by Various Organic Compounds[a]

Compound	Max poss ozone, ppm	Av ozone for 99% reaction, ppm	Ozone peak value, ppm	Av O_3, NO = 5 ppb	Cpd left at O_3 max, ppm
1,2,4-Trimethyl benzene	21	16.06	19.42	3.26	0.020
m-Xylene	18	13.25	16.25	1.94	0.027
Toluene	15	8.60	11.04	0.28	0.123
Benzene	12	6.72	8.35	0.21	0.129
trans-2-Butene	12	9.24	11.49	3.57	0.009
Propene	9	6.54	7.77	0.66	0.039
Ethene	6	3.30	3.97	0.093	0.142
Acetylene	5	0.27	0.75	0.004	0.634
n-Butane	13	6.46	8.02	0.18	0.167
Ethane	7	0.74	1.70	0.011	0.503
Methane	4	0.01	0.05	0.0002	0.946
Butyraldehyde	11	7.95	9.56	0.83	0.038
Propionaldehyde	8	5.78	6.97	0.60	0.038
Acetaldehyde	5	3.61	4.34	0.38	0.038
Formaldehyde	2	1.44	1.73	0.15	0.039
Carbon monoxide	1	0.05	0.14	0.0007	0.638

[a] Based upon 1 ppm compound.

Time to O_3 Peak Value and O_3 Peak Value. The time to the O_3 peak value was derived by taking the derivative of Equation 14, setting the resultant expression equal to zero, and solving for t. The following expression was obtained and was used to calculate the time to O_3 peak value. These values are tabulated in Table II.

$$t_{O_3\,\text{peak}} = \frac{\ln k_a(\text{OH}) - \ln 1.6 \times 10^{-3}}{k_a(\text{OH}) - 1.6 \times 10^{-3}} \qquad (18)$$

The O_3 peak value was then calculated by substituting the time to O_3 peak into Equation 14. These O_3 peak values are tabulated in Table III. These values are extremely high. Since no such O_3 concentrations have ever been observed either in the atmosphere or in smog chambers, it was decided to note what effect a small but measurable quantity of NO would have on O_3 production. With NO at a constant value of 5 ppb, Equation 19 was derived.

$$\langle O_3 \rangle = \frac{n'[k_a(\text{OH})]^2}{4.6[0.107 - k_a(\text{OH})]} \times \left(\frac{1}{k_a(\text{OH})} - \frac{1 - e^{-0.49/k_a(\text{OH})}}{0.107}\right) \qquad (19)$$

With this equation, column 5 of Table III was obtained.

Ozone Forming Potential

The ozone concentration produced by the reaction of 1 ppm of organic compound was significant in each case except for methane. In each case (except for methane), the air quality standard for ozone is exceeded. Put on this basis, all hydrocarbons (except methane) or organic compounds need to be controlled. However, the degree of control is obviously not only dependent upon the parameters used to derive this ozone-forming potential but also on the meteorology that would affect the rate destruction of ozone and the diffusion of the HC. As discussed earlier, the dry deposition rate for ozone can be significant depending upon the particular diffusion rate that is considered for different atmospheric conditions. The O_3 values given in columns 3 and 4 of Table III are upper limit values, i.e., if no deposition is occurring and all of the ozone produced remains in a box type atmosphere. In actuality, as shown in column 5 of Table III, in the presence of NO_x these O_3 concentrations are never realized either in the atmosphere or in smog chambers. Ozone produced from the photolysis of NO_2 is governed by the expression $O_3 = K(NO_2)/NO$. We chose to ignore the reaction of ozone with NO largely because the reactivity scale was derived to be independent of the hydrocarbon/NO_x ratio. If a large quantity of NO_x were employed, for example, then little O_3 would be produced even though the organic compound would eventually (but more slowly) be consumed. However, if too little NO_x were used, then the chain terminating steps involving NO_x eventually would remove all the NO_x from the system, and no further production of O_3 or organic compound degradation would occur.

Therefore, how does one establish a reactivity scale that is applicable in the real world where the HC/NO_x ratio is variable? Obviously, one can write a model for various organic compounds and at various cpd/NO_x ratios and arrive at a list of O_3 concentrations that one can expect at different HC/NO_x ratios for every compound. Such a table would probably be valuable, but again, since new inputs (emissions) are always being introduced, the basic question remains, which cpd/NO_x ratio does one employ when the reactivity or O_3 forming potential of a compound is desired? Also, the presence of aerosols and dry deposition in the atmosphere and wall reactions in smog chambers are expected to reduce the ozone levels. The importance of wall reactions in a chamber is more important than the photolysis of O_3 (*16*). The O_3 values given in Table III are not meant to show ozone levels that are to be expected by the photooxidation of a particular organic compound with NO_x. Instead, the table shows the O_3 formation potential of the compound.

Exact experimental verification for the proposed reactivity scale is not possible since most chamber studies have been done with short irradiation times (3–6 h) and usually employ rather high NO_x concentrations. Some recent studies were performed to qualitatively test the hypotheses that a saturated hydrocarbon (*n*-butane) could produce significant concentrations of ozone comparable to a moderately reactive olefin (ethylene). After 30 h of irradiations, HC/NO_x ratios of 20 resulted in higher average ozone concentration for *n*-butane than for the ethylene.

Table IV shows the ozone-forming potential of compounds when put into five arbitrary classes. This table shows some interesting points when compared with the Dimitriades reactivity scale (Table V). Class I has essentially the same group of unreactive compounds, methane, ethane, and acetylene in both scales. However, the Dimitriades scale also contains benzene, whereas in the proposed theoretical scale, this compound appears in Class IV. Again, it must be emphasized that the aromatics cannot be modeled properly since the degradation products are known. The most reactive hydrocarbons, the internally double-bonded olefin, and the trialkylbenzene are in the most reactive class in both scales.

A reactivity scale could also be based on peak ozone concentration. Depending upon where the group divisions are made, there is not a significant change in the order to reactivities. The only compounds that change order are propene and *n*-butane. Of the 15 compounds investigated, the *n*-butane is ninth in reactivity, and propene is tenth when the 99% HC reaction is used. When the ozone peak is used, these two compounds shift positions. We believe that a reactivity scale based on 99% reaction of the organic compounds is a better indication for basing reactivities. In Table III, for example, are given the concentrations of the various organic compounds at the point where the O_3 maximum has been reached (column 6). Although the fast reacting organic compounds are essentially gone at t_{O_3} max, some of the slower reacting ones are not. At the t_{O_3} max, only approximately 84% of the *n*-butane has reacted. For ethane, only 50% has reacted. Carbon monoxide has reacted only 36%. Therefore, these organic compounds can still have considerable potential in producing ozone if they have not been dissipated. For this reason, a reactivity scale based on 99% compound reaction is more useful.

Table IV. Reactivity Classification Based on Ozone Formation Potential

Class I, <1 ppm	Class II, 1–4 ppm	Class III, 4–6 ppm	Class IV, 6–8 ppm	Class V 8–16 ppm
Carbon monoxide	Formaldehyde	Propionaldehyde	*n*-Butane	*trans*-2-Butene
Methane	Acetaldehyde		Propene	*m*-Xylene[a]
Acetylene	Ethylene		Butyraldehyde	1,2,4-Trimethyl benzene[a]
Ethane			Benzene[a]	Toluene

[a] The aromatics could not be modeled since the degradation products are unknown. They may not be in the particular classification shown for this reason.

Table V. Reactivity Classification of Organics[a]

Class I, nonreactive	Class II, reactive	Class III, reactive	Class IV, reactive	Class V, reactive
C_1–C_3 paraffins	Mono-*tert*-alkyl benzenes	C_{4+}-paraffins	Primary and secondary alkyl benzenes	Aliphatic olefins
Acetylene	Cyclic ketones	Cycloparaffins	Dialkyl benzenes	α-Methyl styrene
Benzene	*tert*-Alkyl acetates	Styrene	Branched alkyl ketones	Aliphatic aldehydes
Benzaldehyde	2-Nitropropane	*n*-Alkyl ketones	Primary and secondary alkyl alcohols	Unsaturated ketones
Acetone		Primary and secondary alkyl acetates	Cellosolve acetate	Diacetone alcohol
Methanol		*N*-methyl pyrrolidone	Partially halogenated olefins	Ethers
tert-Alkyl alcohols		*N,N*-dimethyl acetamide		Cellosolves
Phenyl acetate				
Methyl benzoate		Partially halogenated paraffins		
Ethyl amines				
Dimethyl formamide				
Perhalogenated hydrocarbons				

[a] Reactivity scale proposed by Dimitriades (*4*).

Although this reactivity scale is not perfect, we believe that it could be used to complement that proposed by the use of smog chamber data. The proposed scale is valid not only in the center city but also in rural areas. If control strategies are planned based on the reactivities similar to those given in Table III, the goal to achieve significant reductions in oxidant levels both in center cities and rural areas will be met but may be unnecessary for center cities.

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Determination of Sulfur Dioxide in Stack Gases by Ultraviolet Absorption Spectrometry

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■ Sulfur dioxide was collected and concentrated by bubbling stack gases through a buffered solution of sodium tetrachloromercurate. Treatment with sulfamic acid eliminated interference by nitrogen dioxide. The tetrachloromercurate samples were injected into a reaction vessel containing 15 ml of 1.8 M H_2SO_4 to evolve sulfur dioxide. Design of the reaction vessel is discussed. The SO_2 was carried by a nitrogen stream to an absorption cell mounted in the light path of an atomic absorption spectrophotometer. Molecular absorption measurements were made at 210 nm with a bandwidth of 6.8 nm, using a hydrogen hollow cathode lamp as a source of continuum radiation. The method was sensitive to concentrations as low as 2 μg SO_2/ml in solution, or 3 mg SO_2/m^3 in air, based on a 20-l. air sample.

Sulfur dioxide is one of the most prevalent forms of air pollution. It is released into the air primarily from the combustion of coal and petroleum, the smelting of sulfur-containing ores, production of sulfuric acid, and the paper manufacturing industry.

Several instrumental finishes have been developed for the analysis of SO_2 after an air sample has been scrubbed through an appropriate solution to form sulfite or sulfate. These include the polarographic (*1, 2*), conductometric (*3, 4*), coulometric (*3, 5*), and colorimetric (*6–9*) finishes. In the West and Gaeke method, which is endorsed by the Environmental Protection Agency as the reference method for determination of SO_2 in ambient air (*6, 10–12*), SO_2 is removed by bubbling air through a tetrachloromercurate solution, adding acidified pararosaniline dye and measuring absorbance at 548 nm. The method is sensitive to air concentrations as low as 25 μg SO_2/m^3. The UV absorption bands of SO_2 which cover the range from 320 nm into the vacuum ultraviolet have also been employed for the direct measurement of SO_2 in solution (*13–15*) and in the gas phase (*16*). Instruments for continuous monitoring of SO_2 in stack gases, both by ultraviolet absorption and by various other spectrometric techniques, have also been mentioned in the literature (*3, 17–19*).

In this paper is presented a method for collecting discrete samples of stack gases in an absorbing solution and for completing the analysis by rapid evolution of SO_2 and measurement of molecular absorption at 210 nm by means of an atomic absorption spectrophotometer.

Experimental

Instrumentation. Absorption measurements were made on the Perkin-Elmer 303 atomic absorption spectrophotometer equipped with a recorder-readout accessory and a Sargent 10-mV strip-chart recorder. The spectrophotometer was equipped with a Varian Techtron hydrogen hollow cathode lamp operated at a current of 30 mA. The wavelength was set at 210 nm, and the slit was set at its widest setting which corresponded to a bandwidth of 6.8 nm. The instrument was modified for nonflame cold vapor analysis by removing the burner and replacing it with a flow-through absorption cell. The original apparatus for the evolution of SO_2 has been described (*20*). This apparatus, consisting of a reaction vessel, water trap, and absorption cell, was identical to the setup widely used at the present time for the cold vapor atomic absorption technique of mercury analysis. In the present work, the apparatus for SO_2 evolution and measurement is improved.

Instead of a 15-cm long flow-through absorption cell with quartz end windows (*20*), a simple piece of glass tubing is fitted with an inlet port in the middle and is positioned horizontally in the light path of the spectrophotometer. The glass tube is 17 cm long, 17 mm i.d., and has no end windows. The elimination of end windows prevents very gradual condensation of moisture inside the absorption cell and gradual decrease in signal intensity. Furthermore, the absorption cell becomes flushed with carrier gas more rapidly after an injection, decreasing the time required for the signal to return to the baseline.

The improved SO_2 evolution vessel (Figure 1) has a total internal volume of 60 ml. Compared to the 250-ml internal volume of the original reaction flask (*20*), the new design decreases considerably the extent of dilution with carrier gas that a given amount of evolved SO_2 undergoes and results in better absorption signals and improved sensitivity. The additions of a stopcock at the bottom of the reaction vessel and of a reagent reservoir on a sidearm reduce significantly the time required between successive analyses. The procedure for using the SO_2 evolution vessel is described later under the Analysis section.

A Research Appliance Co. stack gas sampler Model 2373 was used to collect samples. The stack sampler train includes a 5.5-ft long probe and four midget bubblers connected in series and equipped with coarse glass frit dispersion tubes. These are followed by a drying tube, a pump, a rotameter, and a dry gas meter. The probe lining and the entire train of the sampler are made of glass.

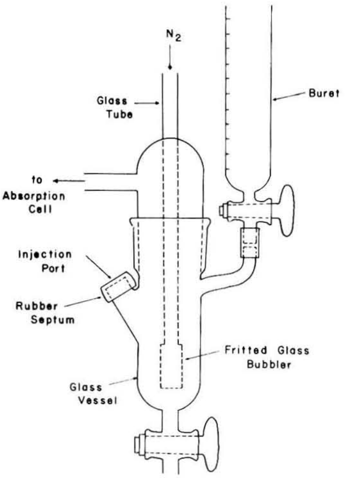

Figure 1. New reaction vessel for SO_2 evolution

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Solution injections into the reaction vessel were made with a Hamilton 1-ml syringe. Compressed nitrogen was used as carrier gas and was regulated by a Matheson flow meter.

Reagents. All reagents were analytical grade, and solutions were prepared using deionized water. The 0.100 M sodium tetrachloromercurate (TCM) absorbing solution contained 11.7 g NaCl and 27.2 g $HgCl_2$/l. Buffered tetrachloromercurate absorbing solution contained, in addition, 84.8 g Na_2CO_3/l., and its pH was adjusted to approximately 8 by addition of HCl.

A standard sulfite stock solution containing 10 000 μg SO_2/ml was prepared by diluting 7.510 g of sodium metabisulfite (98.7% pure) to 500 ml with water containing 5% glycerol. The solution was stored in a polyethylene bottle at 5 °C. The precaution of adding glycerol and refrigerating was taken because simple aqueous sulfite solutions are very susceptible to oxidation and are consequently very unstable. Working standards in the range from 50 to 2500 μg SO_2/ml were prepared by dilution with 0.100 M tetrachloromercurate (TCM).

A standard nitrite stock solution, 8200 μg NO_2/ml, was prepared by diluting 6.343 g $NaNO_3$ to 500 ml with 0.100 M tetrachloromercurate. Working standards in the range from 300 to 7000 μg NO_2/ml were prepared by dilution with 0.100 M tetrachloromercurate (TCM).

Procedure. *Sample Collection.* Samples were collected at a local power plant. Since the probe of the stack gas sampler, which was inserted into the side port of the stack, was only 5.5 ft long, this did not allow samples at various places in the traverse of the sampling area of the stack to be taken; thus, an estimation of total SO_2 released by the particular stack is not possible from these experiments. But the applicability of the analytical finish to real-life stack gases is proved.

A Pyrex wool filter was inserted into the end of the probe to screen out particulates. Fifteen-ml aliquots of saturated sulfamic acid solution were placed into each of the first two bubblers. Fifteen-ml aliquots of buffered 0.100 M TCM solution were accurately pipetted into each of the third and fourth bubblers. Stack gases were pumped through the train at a constant rate of 0.80 l./min until 10–30 l. had been sampled. After each sample was collected, the solutions in the third and fourth bubblers were combined, placed into a labeled polyethylene bottle, and saved for analysis. The absorbing solutions and the sulfamic acid solutions were replaced with fresh aliquots, and the Pyrex wool filter was replaced.

Analysis. Nitrogen carrier gas continuously flowed through the reaction vessel and through the absorption cell at a rate of 1.5 l./min. One-ml aliquots of the samples or standards were injected into the reaction vessel containing 15 ml of 1.8 M H_2SO_4 through a sidearm port covered with a rubber septum. The evolved sulfur dioxide was carried by the nitrogen stream to the absorption cell mounted in the light path of the spectrophotometer. Upon emerging from the ends of the absorption cell, the gas was vented into the hood. For each sample injection, relative absorption was recorded as a function of time. The relative absorption signal increased sharply to a maximum and decreased gradually as the SO_2 dissipated from the system (Figure 2). In the interest of saving time, as soon as the absorption maximum was passed, the reaction vessel was drained and replenished with a fresh 15-ml aliquot of acid solution from the buret. After recording a short portion of the baseline, the next sample was injected and the resulting signal recorded. Relative absorption was measured as the height of the recorded peak above the baseline, and evaluation was made by comparison to calibration curves obtained with standard sulfite solutions.

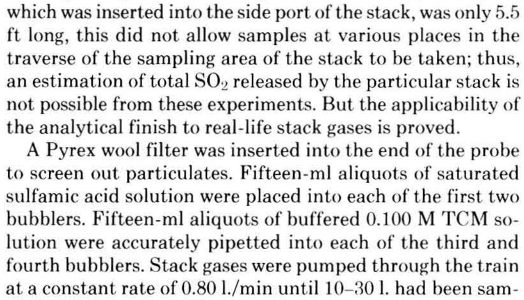

Figure 2. SO_2 absorption signals obtained with old and new reaction vessels

Curve a: signal from injecting 50 μg SO_2 into old reaction vessel. Curve b: from 50 μg SO_2 using new reaction vessel without draining. Curve c: from 50 μg SO_2 using new reaction vessel with draining as soon as signal maximum is passed

Results and Discussion

Decreased Analysis Time with New Reaction Vessel. The design of the reaction vessel illustrated in Figure 1 has distinct advantages over the old reaction vessel (*20*) which was in the form of a 250-ml round-bottom flask. Because of the new vessel's smaller volume and because the acid solution can be drained and replaced quickly, the time required per analysis is reduced to about 30 s. This improvement is illustrated in Figure 2. Since the internal volume of the new reaction vessel is much smaller, the evolved SO_2 is carried to the absorption cell much more rapidly and with less dilution, resulting in a larger absorption signal. Also, because of the reduced volume, the SO_2 is flushed out of the system more rapidly, causing the residual absorption signal to decay more quickly. Furthermore, since the new reaction vessel can be quickly drained through the bottom stopcock and the acid solution replaced, the pen can be returned to the baseline almost immediately after the absorption maximum is passed. That some SO_2 becomes discarded with the acid solution is without any significance because the efficiency of SO_2 evolution is very constant and reproducible under constant experimental conditions.

Reproducibility. Repeated injections of 1-ml aliquots of standard sulfite solutions resulted in relative average deviations from the mean ranging from 0.85 to 7.5% for sulfite concentrations ranging from 4000 to 3.5 μg SO_2/ml. For example, 10 injections of 780 μg SO_2/ml resulted in a relative average deviation from the mean of 1.8%.

Detection Limit. The detection limit of the technique was 2 μg SO_2, since the injection of 1 ml of 40 μg SO_2/ml sulfite standard yielded a signal 40 times the size of noise. This corresponds to a detection limit of 3 mg SO_2/m^3 of stack gases, based on a 20-l. gas sample. The linear range of the calibration curve extends to about 200 μg SO_2/ml, but the curve can be used with precision up to concentrations of at least 2000 μg SO_2/ml.

Optimization of Experimental Variables. The carrier gas flow rate was varied from 0.4 to 3.0 l./min and caused a total absorption signal variation of only 8% with almost constant reproducibility. For convenience, a flow rate of 1.5 l./min was selected.

Although H_2SO_4 concentrations below 1.8 M also released SO_2 from sulfite, signal height gradually decreased with lower concentration of acid. Thus, 0.1 M H_2SO_4 yielded a signal 14% smaller than that obtained with 1.8 M H_2SO_4, and at 0.001 M H_2SO_4 the signal was decreased by 40%. It is reasonable to expect that even at lower acid concentrations, as long as the acid was in excess, the area under the absorption signal should remain proportional to the amount of SO_2 present. However, since dilution decreases the rate of SO_2 evolution, it is much more convenient to use higher H_2SO_4 concentrations (1.8 M was selected) and to measure only the height of the absorption signal. It was noted that the exact volume of acid added to the reaction vessel had an effect on the SO_2 absorption signal intensity; therefore, a constant volume of 15 ml was used in all experiments.

Incorporation of Buffer in Absorbing Solution. Scoggins (*13*) reported a 99% recovery when 2.33 mg of SO_2 was absorbed from a stream of nitrogen carrier gas in 25 ml of 0.100 M TCM absorbent at a flow rate of 0.75 l./min. A study was made to determine the effectiveness of tetrachloromercurate solution as an absorber for higher concentrations of SO_2 expected in stack gases. The outlet port of the reaction vessel was connected via Tygon tubing in series to a glass dispersion tube, a flow meter, and the inlet to the pump of the air sampler. Into the reaction vessel were injected different volumes of the 10 000 μg SO_2/ml sulfite stock solution. For each sample injected, the sampler pump was allowed to draw the evolved SO_2 out of the reaction vessel and through 50 ml of 0.100 M TCM for at least 10 min at a flow rate of 0.80 l./min. Standards were prepared by diluting the 10 000 μg SO_2/ml standard sulfite stock solution with 0.100 M TCM to match the expected concentrations of the absorbed samples, assuming 100% absorption efficiency. The prepared samples and standards were then analyzed by the proposed technique, with the results indicated in the first three columns of Table I. The results indicate that as the amount of SO_2 absorbed increases, the absorption efficiency of the 0.100 M TCM decreases. Also, as would be expected, the pH of the resulting solution decreases with increasing amounts of absorbed SO_2. Thus, after absorption of 200 μg SO_2/ml, the pH is 2.21; after absorption of 1270 μg SO_2/ml, the pH is 1.65. The drop in pH is expected due to the following reaction:

$$HgCl_4^{-2} + SO_2 + H_2O \rightleftharpoons HgCl_2SO_3^{-2} + 2\,HCl$$

Rose (*15*) improved the absorption efficiency of tetrachloromercurate by using a phosphate buffer system at pH 8.3. The present workers made 0.100 M TCM also 0.8 M in sodium carbonate and adjusted the pH to 8 by adding HCl. The resulting concentration of bicarbonate is 10 times concentrated enough to stabilize the pH of a 2500 μg SO_2/ml sulfite solution. With this buffered absorbing solution, the absorption efficiency study was repeated, and the results are presented in the last two columns of Table I. Absorption efficiency improves drastically in the presence of buffer.

Nitrogen Dioxide Interference. Nitrogen dioxide exhibits absorption bands in the region of the near UV absorption bands of SO_2 (*16, 21*). Nitrogen dioxide is present in coal combustion stack gases at concentrations on the average about ⅓ as high as the SO_2 concentrations (*22*). Nitrogen dioxide becomes absorbed by the tetrachloromercurate absorbing solution and readily released upon injection into the reaction vessel containing acid. The relative absorption of SO_2 and NO_2 species is illustrated by the calibration curves in Figure 3. The absorption due to SO_2 was about 23 times more intense than that due to nitrogen dioxide at the 210-nm analytical wavelength.

The interference of nitrogen dioxide in the SO_2 determination is not a simple enhancement of the SO_2 absorption signal. When sulfur dioxide is bubbled through tetrachloromercurate, followed by nitrogen dioxide, the signal expected

Table I. Effect of Buffer upon Efficiency of SO_2 Absorption by Tetrachloromercurate

Concn prepd by diln, μg SO_2/ml	Concn absorbed by unbuffered TCM, μg SO_2/ml	% Absorption efficiency	Concn absorbed by buffered TCM μg SO_2/ml	% Absorption efficiency
200	200	100	192	96
400	400	100	366	91
800	720	90	738	92
1200	980	82	1206	100
1600	1115	70	1593	100
2000	1270	64	1956	98

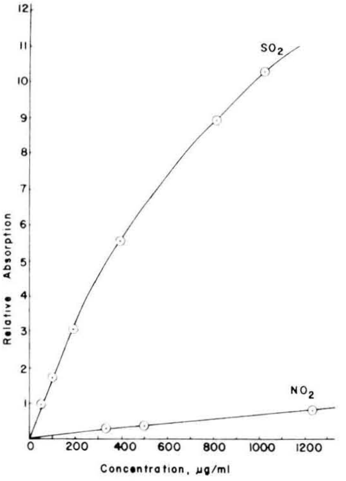

Figure 3. Calibration curves for SO_2 and NO_2 at 210 nm

Table II. Effect of NO_2 Interference on SO_2 Absorption Signal and Elimination of NO_2 Interference by Sulfamic Acid

Wt of SO_2 absorbed, mg	Wt of NO_2 absorbed, mg	Rel absorption, chart units
In 0.100 M tetrachloromercurate, unbuffered		
10	0	19.5
10	82	0.0
100	0	64.2
100	82	33.4
In 0.100 M tetrachloromercurate, buffered		
10	0	17.7
10	82	13.1
100	0	65.5
100	82	43.3
Bubbled through sulfamic acid prior to absorption in buffered 0.100 M tetrachloromercurate		
10	0	17.7
10	8	18.2
10	41	18.6
10[a]	0	17.8

[a] Prepared by dilution of sulfite standard.

Table III. Results of Determination of SO_2 in Stack Gas Samples

Sample no.	Sample vol, l.	Concn in soln, μg SO_2/ml		Concn in air, μg SO_2/m^3 x 10^5		% Diff
		West & Gaeke	UV absorption	West & Gaeke	UV absorption	
1	7.71	154	135 ± 2	5.99	5.25	12.3
2	7.71	96	84 ± 2	3.74	3.27	12.6
3	7.42	91	70 ± 3	3.68	2.83	23.1
4	3.14	91	93 ± 3	8.69	8.88	2.2
5	14.3	163	163 ± 7	3.42	3.42	0.0
6	14.3	133	134 ± 5	2.79	2.81	0.7
7	20.0	66	69 ± 6	0.99	1.04	5.0
8	20.0	...	63 ± 8	...	0.94	...
9	17.1	...	40 ± 5	...	0.70	...
10	25.7	62	60 ± 3	0.72	0.70	2.8
11	20.0	68	75 ± 8	1.02	1.12	9.8
12	11.4	22	29 ± 2	0.58	0.76	31.0
13	28.6	152	159 ± 13	1.59	1.67	5.0
14	22.9	137	141 ± 11	1.79	1.85	3.4

for SO_2 is greatly diminished (Table II). The presence of the bicarbonate buffer reduces but does not remove the interference. Sulfamic acid has been mentioned in the literature *(12)* as a means of removing nitrogen oxides which, when present in concentrations exceeding 2 ppm in solution, cause a fading of the red-violet color in the West and Gaeke pararosaniline method for SO_2. Sulfamic acid is expected to decompose nitrite to nitrogen gas. The effectiveness of sulfamic acid was tested by the following experiment. Two reaction vessels containing acid solution were connected by separate dispersion tubes into a common vessel which contained the saturated sulfamic acid solution, and then to an impinger with 30 ml of buffered TCM absorbent. Simultaneously, aliquots of standard sulfite were injected into one reaction vessel and aliquots of standard nitrite into the other reaction vessel. The absorbent solution was then analyzed and compared to a standard (Table II). These results indicate that sulfamic acid is indeed effective in eliminating the nitrogen dioxide interference. Naturally, in the actual stack gas samples, any interactions between SO_2 and NO_2 prior to contact with the first solution in the sampling train are of no concern because they would also be occurring inside the stack. But interactions in the absorbing system seem to be eliminated by sulfamic acid.

Results of Stack Gas Analyses. Samples were collected as described under the Procedure section and were analyzed by quadruplicate injections and comparison to a standard calibration curve. The samples were taken from a single stack at different times. The samples were also analyzed by the West and Gaeke pararosaniline method *(11)*. The latter required a 2–100 dilution of the samples and the standards to lower the concentrations to the range where the method is applicable. The results of both sets of determinations are listed in Table III. The average deviation from the mean for repeated injections is indicated for the concentrations of SO_2 found in the test solutions by the proposed method. The results show favorable agreement between the two methods for most of the samples. Some deviation may be attributable to volumetric errors generated in successive dilutions of samples for the pararosaniline method.

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Sampling for Contaminants in Ecological Systems

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■ A framework for designing schemes to sample for contaminants requires a clear statement of objectives, selection of an appropriate model and error system, and should yield cost-effective ways to sample to meet specific objectives. After reviewing five classes of models that might be used in studies of contaminants, we conclude that a universal model is presently out of reach, but that existing systems will serve various practical purposes. A rationale for choice of error structure leads to such frequency distributions as the gamma and lognormal; therefore, we have devised ways of testing the major assumption involved—that of constancy of the coefficient of variation. The above framework yields a revised optimum allocation and sample-size formula. Our study of models leads to recommending the use of body size (length, weight) as an auxiliary variable in sampling for either estimation (double sampling) or comparisons (analysis of covariance). A technique now used in industrial experimentation is recommended for sampling for model building (or model fitting), and it is suggested that techniques in use in economic geology also be considered for adaptation.

Environmental "crises" lead to sampling problems in many dimensions and in many forms. An ever-increasing array of chemical agents are regarded as potential threats to man and his living environment. Until we understand the mechanisms and determine the rates governing the behavior of these substances in ecosystems, there can be little real assurance that a given substance does or does not constitute a hazard. Thus, this paper is concerned with problems in assessing the behavior of trace substances introduced into natural systems. Intensive study of radionuclides in food chains during and since the period of worldwide fallout associated with nuclear weapons testing has provided much in the way of technology for studying other contaminants in natural systems and led to the development of the field of radioecology.

Appraisals of hazards and the choice of control measures can use many methods and approaches, not all of them directly relevant here. We mention two such procedures. One is to do bioassays of each new substance to detect those that may be hazardous to life and to then either introduce suitable safeguards or prohibit use of the chemical in question. The second precaution depends on careful surveillance of the immediate environment and diets of humans. The assumption is that if man's health is protected, the substance in question is not a real hazard in his environment. Such a policy provides no protection against indirect or delayed effects on ecosystems, which may ultimately affect mankind.

Effective planning for any sampling program requires a clear understanding of objectives of the study, delineation of the population to be studied, and some advance information as to the variability that will be encountered in the field. Inasmuch as the behavior of many contaminants in ecological systems is highly dynamic over time, sampling designs must also be directed toward measuring levels that change rapidly in time. A sampling framework specifically geared to time usually has to be supplied as a kinetic model of some kind. Such a model must incorporate a measure of the variability that exists in the system if it is to be used in sampling design. Hence, this paper covers four main topics: objectives, models, frequency distributions, and sampling designs.

Objectives in Sampling for Contamination

Sampling methodology for dealing with contaminants and pollutants has generally lacked the sharp focus existing in studies of natural resources. That focus is the emphasis on efficient exploitation, which translates readily to questions of "how much?" or "how many?" and thus permits direct application of sample survey methods. Success in resource management can be appraised in terms of yield or harvest. The following paragraphs suggest some objectives in sampling for contaminants and pollutants.

Estimation of Material Balance. The main goal of such a survey may be taken to be the estimation of the total amount of some substance (for example, DDT) in the environment. If the primary objective is actually one of estimating the total amount present, the quantities found in the biota will then be of minor importance. This is simply because the mass of the biota is a very small fraction of the mass of the biosphere. The bulk of DDT residues, for example, are usually found to be in the atmosphere, suspended in water, or in surface soils and river silts. The biota are, furthermore, probably not important quantitatively in their effect on large-scale transport and distribution of most contaminants. Efficient allocation of samples for the establishment of a material balance is thus likely to include relatively few samples of living material.

Establishment of Baselines for Monitoring. Since public concern with substances like DDT has mostly to do with potential effects on living systems, actual surveys may be planned along the lines of what have been described as "baseline" studies. Sampling objectives then have to do with measuring changes in concentrations over time, and since the major emphasis will now be on the biota, a large fraction of the sampling effort may be devoted to biological material. However, it is also desirable to plan such surveys for eventual use in predicting *future* concentrations, and thus necessary to incorporate measurements on the major reservoirs ("air, earth, and water") as well.

The available evidence points to distinct seasonal cycles in concentration of contaminants in the biota. Such changes may be due to seasonal changes in environmental conditions. At the present we do not know what seasonal shifts may occur in the main transport routes. For pesticides, there obviously are sharp seasonal peaks in application, and stream transport presumably might have another seasonal peak during maximal flow periods. If the stratosphere is involved in atmospheric transport, then analogy with fallout radionuclide phenomenology would indicate a spring peak in fallout of the transported material. Although precise definition may be lacking, present knowledge certainly seems sufficient to require that any sampling scheme be carefully designed to reflect seasonal changes.

Given a baseline, there follows a need for monitoring to determine what changes occur. A major practical problem with monitoring schemes is that they necessarily involve a routine, which can cause those responsible for operations to lose sight of the objectives. A sufficiently thorough baseline survey may make it possible to limit monitoring activities to a level at which high quality can be sustained.

Assessment of Consequences of Pollutants on Human Health. It is conceptually possible to sample for contaminants

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to obtain data for direct use in a quasi-epidemiological study. For example, there are a number of recent claims of "statistically significant" evidence of long-term damage to the health of humans from various sources of pollution (largely of atmospheric origin). Many of the claims rest on some sort of multiple regression analysis with "health" parameters as dependent variables. Some examples and references are in the Proceedings of the Sixth Berkeley Symposium on Mathematical Statistics and Probability, Volume VI (*1*).

One approach to a scientific understanding of effects on health is to require that any postulated mechanism for damage be one that can be tested for in the laboratory. The difficulty then becomes that of extrapolating from levels that do demonstrable damage in the short-term experiments usually feasible in the laboratory down to the effects that *might* result at the much lower levels to be realistically expected. Another problem is that of extrapolation from test animals to man.

The relationship between low levels of chronic pollutants and effects on human health is obviously a complex one, and one not likely to be soon understood.

Understanding of Environmental Systems. In ecology, it is seldom feasible to consider the "health" of an individual. We are instead concerned with the well-being of populations. In assessing the effect of some pollutant on natural populations, one may thus need to study a sequence of phenomena, beginning with the kinetics of the contaminant in food chains, progressing through the dose-response relationship exhibited by individuals, and terminating in a possible effect on the population dynamics of the species of interest. We note that the dose-response relationship in nature may well be different from one obtained under laboratory conditions.

The point of view adopted here is one of a need to understand the system under study. In consequence of the complexities of ecosystems and limited knowledge, it is not practical to expect to do extensive population studies in search of effects of pollutants at levels far below those causing any known consequence to individuals under experimental conditions. It is, however, feasible to determine the fate of such substances in natural systems, as insurance against as yet unknown conditions or hazards. Any policy that assumes no damage in the absence of lethal effects in the laboratory is obviously a risky one. DDT provides a prime example in that rather high tissue concentrations are required to evoke a toxic response in individuals. Thus, proponents of the unrestricted use of DDT were able to point to laboratory data showing "nontoxicity" at levels higher than usually found in nature. But it was subsequently discovered that much lower levels of a degradation product of DDT interfere with calcium metabolism in birds, causing thin eggshells and reproductive failure. Furthermore, by not knowing what happened to DDT in an ecosystem, investigators tended to look for trouble in the wrong species, and it was only after the near decimation of a rare species actually occurred that a link with pesticides was inferred. In point of fact, there still are few, if any, definitive studies of food chain kinetics of DDT, in spite of warnings given by some foresighted wildlife managers as early as 1945. In addition, so little is known about the global kinetics (that is, the mechanisms, pathways, rates, etc., of transport of DDT over the earth's surface) that there are as yet insufficient grounds for making predictions about the ultimate fate of the 2 million metric tons already released into the biosphere (*2*).

Objectives in sampling thus become anything but clear-cut at this level of complexity. Models provide convenient summaries of what has been learned, and once a particular model is established as a suitable representation of the available data, there is then considerable interest in the comparative study of parameters. The appropriate sampling methodology thus seems to be more nearly that of "analytical" sampling. Cochran (*3*) distinguishes analytical sampling as having to do with comparisons concerned with forming and testing hypotheses, as opposed to descriptive sampling in which the objectives have largely to do with obtaining descriptive information. Sedransk (*4–6*) describes the use of several survey techniques (double sampling, cluster sampling, and sequential sampling) for analytical purposes.

Models

We devote a substantial amount of space to models here, on the grounds that we do not believe that highly dynamic systems can be effectively or efficiently sampled without good models. From the analytical point of view, sampling may be considered as being a tool for model building. The models, in turn, summarize our understanding of the system, from which knowledge decisions must be made.

There is a tendency for the scientist with a traditional laboratory orientation to suppose that the first priorities should go to careful experimental studies, from which models might then be devised, if necessary. Unfortunately, too much of the laboratory work done thus far has not been planned with field problems in mind. Operating temperatures, species, body size, methods of administration of the test substance, and sampling times have all been carefully standardized, thus eliminating the sources of variability found in nature. Although better experimental design will help on this score, we feel that enough is now known about the general nature of the input-output models relevant to the field situation, that selected models ought also to be used in designing both field and laboratory work.

Our approach in this section is one of discussing potential models and pointing out the features that seem not to be in accord with what is known about kinetics of various contaminants in ecosystems. While we are not able to recommend a universal model, it does seem that certain choices will be much more realistic and useful than others.

Compartment Models. A basic approach is to view the ecological system in terms of inputs and outputs and to focus on single components of the system insofar as possible. The building block for modeling is thus a component (conveniently an individual organism) with an input and output:

$$\xrightarrow{\lambda}\boxed{\;y(t)\;}\xrightarrow{\mu y(t)}$$

where $y(t)$ represents the current burden (content) of some substance at time t, λ is an input (here considered constant over time), and μ is the fraction of current burden lost (output) in a unit of time.

Given such a simple structure, a differential equation model and solution are immediately available:

$$\frac{dy}{dt} = \lambda - \mu y \qquad y = \frac{\lambda}{\mu}\left[1 - e^{-\mu t}\right] + y(0)e^{-\mu t} \tag{1}$$

where $y(0)$ is the initial condition (body burden at the time observation begins). This "uptake and retention" equation is widely familiar in various contexts in a number of fields but has rarely been fit to actual data on contaminants in ecological systems.

Components of a large system may be conveniently represented by boxes and interconnecting arrows. The boxes may, of course, represent quite diverse entities ranging from a source of contamination (which may in turn range from stratospheric fallout to a sewer pipe) to the ultimate consumer in a food chain. There is a large biomedical literature devoted to these "compartment" models, with several books [e.g., Sheppard (*7*) and Atkins (*8*)] providing summaries of methodology and applications (largely "tracer" studies in biomedical research). For a recent example, see Metzler (*9*).

In ecological applications the model conveniently starts out with some source that introduces a contaminant into the environment of a living organism (usually a plant) which becomes contaminated and is then consumed by an animal and so on up the food chain. Considerable difficulties are introduced by uncertainties about the interconnections in the system (in particular, questions as to the food habits of various species). In aquatic systems there are also often questions as to the role played by the aqueous environment, i.e., contaminants may often be taken up directly from the water as well as ingested in food. Plants (including algae and phytoplankton) may acquire burdens of many substances through adsorptive processes (essentially attachment to surfaces) as well as through absorption (passage into cells and interior regions).

Simplifying System Models. Perhaps the major problem in using a system of differential equations to model a food chain is that it is usually not possible to assume constancy of various coefficients over time. Quite rapid changes in "transfer coefficients" (which represent transfer of the contaminant from one "box" to another) may be difficult to model accurately and may also lead to an analytically insoluble system of equations. Our working approach thus far has chiefly been via difference equations evaluated on a computer, both as a matter of convenience and in consequence of a supposition that there are behavioral and physiological grounds to believe that a Δt of one day may be more realistic than a differential.

One serious difficulty in modeling food chain systems is the phenomenon variously known as "feedback" or "recycling." A common example is the prospect that a substance excreted into the environment may eventually reenter the biological system. Other examples include exchanges between tops and roots of plants, and there are, of course, a number of prospects for such exchanges between the various body compartments of a single organism. Such feedbacks can result in great complexity in a system, especially if the rate coefficients may change rapidly in time.

In many circumstances, feedbacks are essentially second or higher order effects and may be neglected in modeling. In terrestrial environments, many contaminants are effectively bound to the soil, so that they are essentially taken out of circulation after excretion (and thus enter a "sink"). Alternatively, it is usually true that any recycling of a contaminant lost from the living elements of the system either by excretion, death, or through leaf-fall, etc., will be considerably delayed in reentry by the length of time required for decomposition, uptake, and so on. One can thus alternatively postulate a "pool" with a very slow turnover which will presumably damp out any oscillations due to feedback.

In aquatic environments a major potential source of rapid feedback seems to lie in the prospect that a contaminant may be taken up directly from the water. Consequently, it might appear that each component of such a food chain has to exhibit a double-arrow connection to a central compartment (the water) in addition to those connections comprising the food chain proper. The effect of such interconnections can, however, be simplified or for short-term investigations be disregarded on the grounds of consideration of relative masses of biota and water. With the exception of laboratory situations (e.g., experiments in aquaria), the mass of the biota is an extremely small fraction of that of the surrounding water. Consequently, the quantities of a contaminant released from the biota in a unit of time may be considered to be of negligible overall importance, and only inputs need be specifically considered, while losses go to a "sink." Such a principle is not, of course, universal, inasmuch as certain ions may be selectively removed and concentrated, a well-known example being phosphorus in lakes. It is also the reason why "model ecosystems" (mostly aquaria) are unrealistic.

Another consequence of the small mass of the biota relative to that of its environment is that models of the kinetics of contaminants can often be structured so that the processes determining distribution and redistribution in the physical environment may serve as "forcing" or "driving" functions for the system of differential equations, making for a convenient and reasonably compact structure.

The actual use of devices like those above evidently requires a good deal of firsthand knowledge of the system along with extensive observations on levels of the contaminant being studied over time. We note that a comprehensive understanding of, for example, feeding relationships ("who eats whom") within a given system is generally *not* available and that securing such knowledge may be very time consuming and expensive.

We now consider some specific structural aspects of food chain models, with the intent of pointing out limitations and circumstances in which the models may be useful.

Linear Differential Equations with Constant Coefficients. The best-known and broadest class of kinetic models is, of course, that of linear differential equations with constant coefficients, which serves as a general framework for the preceding descriptive material. Turner et al. (*10*) discuss a convenient matrix formulation in which the differential equations appear as:

$$\dot{\mathbf{n}} = \mathbf{K}\mathbf{n} \tag{2}$$

with solution:

$$\mathbf{n} = e^{\mathbf{K}t}\mathbf{n}_0 \tag{3}$$

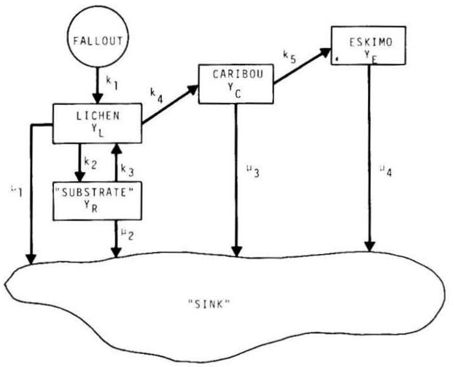
where $\mathbf{n}$ is a vector of observed quantities ("state variables"), i.e., observations on amounts or concentrations of a contaminant in each of the boxes representing a component of the biota, $\mathbf{n}_0$ denotes a vector of initial conditions, the dot notation implies matrix differentiation, $\mathbf{K}$ is a matrix of constant coefficients, and $e^{\mathbf{K}t}$ is a matrix exponential function. Turner et al. (*10*) provide schemes for evaluating the solution, including a particularly convenient method appropriate when the eigenvalues of $\mathbf{K}$ can be considered to be distinct. In practice, a forcing function usually is required, so that Equation 3 becomes:

$$\dot{\mathbf{n}} = \mathbf{K}\mathbf{n} + \mathbf{f} \tag{4}$$

where $\mathbf{f}$ represents a vector of forcing functions (frequently containing zeros in all but the first entry). The result provided by Equation 3 thus corresponds to the general solution of the reduced equations (the "complementary function"). In applications concerned with radioactive fallout (*11*) and DDT (*12*), we have found a negative exponential function useful and seemingly realistic as a forcing function. An example of such a system and the corresponding elements of Equation 4 appear in Figure 1, which depicts our current model of the study reported (*11*) in terms of differential equations.

Our experience suggests that the solutions of sets of equations like Equation 4 will yield poor fits to field data. The main difficulty seems to be that some of the coefficients of the $\mathbf{K}$-matrix are not constants but change in time, often relatively rapidly. One thus must replace such coefficients with functions of time, complicating the model considerably, and often leading to intractable equations. Models with constant coefficients can, however, be quite useful in appraising laboratory studies and short-term field studies. A schematic like that of Figure 1 is extremely helpful in visualizing the system and in beginning to construct a more realistic model.

Linear Differential Equations with Coefficients Functions of Time. In practical work, such equations provide the least complicated model that provides sufficient realism. The coefficients that are usually indicated as changing in time are the transfer coefficients. These changes are often appar-



$$\begin{bmatrix} \frac{dY_L}{dt} \\ \frac{dY_R}{dt} \\ \frac{dY_C}{dt} \\ \frac{dY_E}{dt} \end{bmatrix} = \begin{bmatrix} -(k_2+\mu_1) & k_3 & 0 & 0 \\ k_2 & -(k_3+\mu_2) & 0 & 0 \\ k_4 & 0 & -\mu_3 & 0 \\ 0 & 0 & k_5 & -\mu_4 \end{bmatrix} \begin{bmatrix} Y_L \\ Y_R \\ Y_C \\ Y_E \end{bmatrix} + \begin{bmatrix} k_1Ae^{-Bt} \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

Figure 1. Flow diagram and matrix differential equation model for cesium-137 in arctic food chain

ently due to seasonal shifts in food habits of animals and presumably may also occur with plant growth patterns. It may also be that loss (excretion) rates change in time—we are inclined to assume that such changes may be of minor importance. A simple example of an equation of this class is:

$$\frac{dy}{dt} = -\frac{\mu}{t}y \qquad (5)$$

with solution, $y = y_0(t_0/t)^{\mu}$, a "power function", where t_0 and y_0 pertain to initial conditions. Curves of this form have been interpreted as demonstrating changing loss rates. An alternate prospect is that the system being observed is comprised of several compartments, each having different loss rates, and thus a "spectrum" of coefficients results in a compound excretion curve (*13*).

"Particle" Model. A third class of models deals with the stochastic behavior of individual atoms or molecules in transit through the system and may be conveniently referred to as "particle" models. These models can be described in terms of transition probabilities and difference-differential equations written for the processes being modeled. The basic input-output process then appears as [(*14*), p 414]:

$$P_0'(t) = -\lambda P_0(t) + \mu P_1(t)$$

$$P_n'(t) = -(\lambda + n\mu)P_n(t) + \lambda P_{n-1}(t) + (n+1)\mu P_{n+1}(t) \quad (n \geq 1)$$

where λ now represents the (instantaneous) probability of a single particle entering the system and μ the probability of a particle leaving the system, $P_0(t)$ and $P_n(t)$ refer to probabilities of zero and n changes, respectively, and a prime denotes differentiation.

The mean value of the stochastic process is identical to the solution of the basic differential equation (Equation 1) already given (*14*). Of main interest here is the intuitively plausible result that as the number of particles involved becomes large, the coefficient of variation becomes vanishingly small [as can be shown formally by using probability generating functions, following Feller (*14*), Chap. XVII]. Thus, while the "particle" models are of considerable theoretical interest [and are applicable to a wide variety of other phenomena, cf. (*15–17*)], the usual circumstances with regard to contaminants are such that there are very large numbers of individual particles in the system at any one time, so that variability due to the stochastic process is negligible, and one may as well use the simpler differential equations.

"Mass Transfer" Models. A different kind of stochastic model seems more appropriate to food chain studies. It may be illustrated by considering the ingestion by an animal of a sequence of meals each containing some variable quantity of a particular contaminant. In many cases, the contaminant is transferred to the blood, distributed to various tissues, and gradually excreted. Quite certainly these various processes result in the loss of identity of the individual quantities ingested (presumably the degree of mixing is a function of retention time). If the excretion or other loss process can be considered to proceed at a constant rate, then we can propose a model for body burden (Y) at any given time as:

$$Y = X_1e^{-\mu t_1} + X_2e^{-\mu t_2} + \ldots + X_ie^{-\mu t_i} + \ldots \qquad (6)$$

where X_i represents the quantity of contaminant in a meal ingested at time t_i (t_i represents the time interval between the present and the time of the ith most recent meal), and μ is the loss coefficient. Frequency distributions of the X_i and t_i then determine that of Y. Such models may perhaps be distinguished from the "particle" models by calling them "mass transfer" models. Rustagi (*18, 19*) and Jacquez and Mather (*20*) have proposed models for human body burdens of various contaminants that seem to us to belong in the above general class (but were not so described by the authors above).

Parzen (*21*) terms models of the above type as "filtered Poisson processes", which seems an apt description of the filtering exerted (by passage through an animal) on the compound Poisson process generated by summing random variables separated by time intervals that are also random variables. Under reasonably general conditions, these models have the simple uptake-and-retention model as a limiting case. Of particular importance here, in most cases of practical interest, the coefficient of variation tends to become very much smaller than that of the "meals", i.e., as t_i becomes large:

$$\lim_{t\to\infty} [\text{Coef. var. }(Y)]^2 \to \frac{\mu}{2\nu}\{1 + [\text{Coef. var. }(X)]^2\}$$

where ν is the number of meals per unit time. This is another way to state the generalization that "an animal averages over his food supply". There is, however, evidence [see for example, Eberhardt and Nakatani (*22*)] to show that this precept is not true in the sense that the coefficient of variation of body burdens of a predator does not appear to be much different from that of its prey which, in turn, is roughly comparable to that of its food supply (and so on, including vegetation).

Linear Differential Equations with Coefficients as Random Variables. Our fifth class of models might be termed "population" models, since one of the more direct supporting arguments in practice seems to be that of sampling populations of individuals having different loss coefficients and uptake rates. Such an explanation provides a useful alternative to the "averaging" difficulty described for the previous class of models. Moreover, there is a substantial basis for supposing such intrapopulational differences exist, as described below.

Turner (*23*) and Turner et al. (*10*) provide a specific formulation as the "single-process law". A simple application arises if we consider that the loss rate in the "retention equation", $y = y_0e^{-\mu t}$, has approximately a gamma distribution over a population of individuals such that:

$$f(\mu) = \frac{\beta^{\alpha}}{\Gamma(\alpha)}\mu^{\alpha-1}e^{-\beta\mu} \qquad (7)$$

then we have:

$$E(y|y_0) = y_0 \left(1 + \frac{t}{\beta}\right)^{-\alpha} \tag{8}$$

which is a result given by Turner *(23)* in the form of the "single-process" law. Matis *(24)* also introduces "gamma time-dependency" into a compartment model. When the coefficient of variation of the gamma distribution approaches zero, Equation 8 is indistinguishable from the simple retention equation.

Note that the equation just above denotes the change in average body burden to be expected if one samples a population of individuals over time, and is especially interesting in that it is essentially indistinguishable in practice from Equation 5 [and its stochastic analogue, see Wiggins *(15)*], which represents a very different situation, one in which the loss rate diminishes proportionately to elapsed time. This is another example of the hazards of associating causal mechanisms with a particular form of curve.

Body Size and Models. There is a substantial quantity of experimental evidence to show that excretion rate of many trace substances is proportional to a fractional power of an animal's body weight *(25, 26)*. The logical basis for such a phenomenon seems to be the well-known relationship between metabolic rate and body size, expressed as:

$$y = \alpha w^{\beta} \tag{9}$$

where y is some expression of metabolic activity (e.g., oxygen consumption), α is a "proportionality constant", β is typically less than unity, and w is body weight. Kleiber *(27)* has assembled extensive data that indicate β to be approximately $\frac{3}{4}$.

In most natural populations, body size is an increasing function of age, while the frequency of ages is a (monotonically) decreasing function of age. One is thus led to attempt to use Equation 9 and a growth curve to transform a model for age structure into a model for retention time. A simple example is given by Eberhardt *(26)*. More realistic models apparently lead to difficulties with integration, but it seems a reasonable conjecture that the resulting distribution will be markedly skewed and unimodal, and thus susceptible to approximation by a gamma distribution. In any case, it seems that the above line of argument provides a plausible alternative structure for observed variability in body burdens; i.e., that the variation depends on the size structure of the population instead of, or in addition to, variation in contaminant concentration in the food supply.

There is little experimental data on the relationship of rate of *uptake* of trace substances to body weight, but a number of investigators have found body burdens do increase with age (and hence weight). Eberhardt and Nakatani *(28)* have proposed that retention time should increase in rapidly growing animals, in consequence of Equation 9, which has a negative exponent when retention is involved.

Frequency Distributions

Background. Since many of the kinetic models used for food chain studies are deterministic in nature, some assumption as to error distribution about the model is needed to design field surveys. In practice, it can be anticipated that the fluctuations of data points around the model will be due to stochastic processes, analytical (laboratory) errors, and quite possibly errors in structuring the model.

The common practice of assuming additive and normally distributed error seems to us neither empirically nor logically acceptable. Actual data on radionuclides *(29, 30)* and other contaminants, such as DDT, show skewed frequency distributions and a relatively constant coefficient of variation.

A logical argument against additive error components is just that radionuclides, pesticides, and various other trace elements have been studied over ranges of concentrations that differ by a factor of 10^6 or more. When one observes comparable uptake-and-retention curves from such a range of concentrations, it becomes very difficult to accept a model with additive, normal errors. Since such a model is almost invariably used in present analyses of field data, we think that it is essential to look rather carefully at alternative possibilities that are in accord with what is actually observed in practice.

The gamma and lognormal frequency distributions provide convenient models for the circumstances just described and have been used in various studies of radionuclides [e.g., Ellett and Brownell *(31)*, Schubert et al. *(32)*]. Koch *(33, 34)* has described a large number of applications of the lognormal distribution and discusses the ways in which multiplicative processes leading to the distribution may arise in various contexts. The gamma distribution has been widely applied, both as a flexible, skewed two-parameter model for positive random variables, and in specific contexts. Cox and Smith *(35)* and Cox *(36)* discuss "waiting-time" type applications in queuing and renewal theory. We do not propose to attempt a detailed theoretical argument leading to a specific distributional model for the phenomena considered here. We do note, however, that the input-output processes already described seem somewhat difficult to visualize in a multiplicative context. On the other hand most of the models are composed of exponentials, and an exponential transformation of a normally distributed random variable results in a lognormal distribution.

From the standpoint of the practicing statistician, the lognormal distribution provides a most convenient model, since a logarithmic transformation of the observations permits direct application of normal-theory methods to the transformed data. Our main question thus has to do with those circumstances where lognormality is assumed but the underlying distribution is in fact the gamma distribution. Some useful ancillary information is also obtained by considering the converse situation, i.e., applying statistics appropriate for the gamma distribution when in fact the lognormal holds.

Since we have suggested that the coefficient of variation (c) may be constant from place to place and time to time, our emphasis will be on testing the hypothesis that c is in fact constant. If that hypothesis can be accepted (tests are suggested below), then further analyses (which we will not discuss) can be directed toward comparisons between means. Our interest here is thus in the "scale" parameters, σ^2 (lognormal) and β (gamma distribution).

The s^2 and z Statistics. A logarithmic transformation of lognormally distributed data permits tests of hypotheses about σ^2 based on the sample variance (s^2) of the random variable $y = \log_e x$. As is well known,

$$\frac{\nu s^2}{\sigma^2} \sim \chi^2_{\nu} \tag{10}$$

where ν = degrees of freedom in calculation of s^2. A useful statistic for random variables from the gamma distribution is:

$$z = \log_e \bar{x} - \overline{\log_e x} \tag{11}$$

or the difference between the natural logarithm of the mean of the observations minus the mean of log-transformed observations. This statistic was used (in another context) by Linhart *(37)* who cites Bartlett *(38)* for the characteristic function of z and mentions a proof given by Bartlett and Kendall *(39)*.

Linhart uses Bartlett's approximation to the sampling distribution of z to find confidence limits for the coefficients of variation of a gamma distribution in the form of Equation 7. He gives the approximation as:

$$z \sim \frac{1}{n\beta}\left[1+\frac{1+1/n}{3\beta}\right]\chi^2_{n-1} \qquad (12)$$

and gives some further results on accuracy of the approximation. Using the results given in refs. *37–39*, Eberhardt and Gilbert (*40*) show that for the range of values of the coefficient of variation indicated above as encountered in practice, roughly 20–70%, the above results can further be summarized by tabulating approximate expectations as:

	z	$\dfrac{s^2 = \dfrac{\sum(\log_e x - \overline{\log_e x})^2}{n-1}}{\sigma^2}$
lognormal	$\dfrac{\sigma^2}{2}$	
gamma	$\dfrac{n-1}{n\beta}$	$\dfrac{2}{\beta}$

As a useful rule-of-thumb, the above tabulation can be reduced to a statement that s^2 will be roughly equal to the squared coefficient of variation (c), while z is about one-half of c^2. These several approximations thus serve to make practical decisions for sampling designs.

The z-statistic is also useful in dealing with the problem of "pooling" or compositing samples. Accurate measurements of trace substances are quite expensive so that many investigators combine ("pool") a number of independently collected samples and assay an aliquot of the combined material. Such a sample may thus be regarded as yielding an average value. The z-statistic reflects the difference between the logarithm of a pooled sample and the logarithmic mean of a set of independent samples from the same population. Since, as noted above, the expected value of z is approximately $c^2/2$, it thus becomes possible to judge the difference to be expected between the two procedures for a given coefficient of variation.

The sampling distributions given by Equations 10 and 12 permit F-tests of hypotheses about σ^2 (lognormal) and β (gamma distribution) and thus provide a convenient means for testing the constancy of the coefficient of variation over time or from place to place. Tests on β will necessarily require replacing Equation 12 by a further approximation:

$$z \sim \frac{1}{n\beta}\chi^2_{n-1} \qquad (13)$$

where $\beta \doteq 2/c^2$; the term in brackets in Equation 12 will be nearly unity unless the coefficient of variation is quite large.

To study the behavior of pairwise F-tests based on Equations 10 and 13 on *both* distributions (gamma and lognormal), we ran a series of simulation trials. Lognormal random variables were generated by an exponential transformation of unit normal deviates generated as suggested by Box and Muller (*41*). The gamma distributions were obtained by summing exponential random variables produced by transforming uniform random variables [cf., for example, Naylor et al. (*42*)]. The generators used were subjected to extensive testing along the lines of study by Kronmal (*43*). Sample sizes of 6 and 21 random variables were used, and 1000 pairwise tests were conducted for each entry in Table I. The entries in the table show the approximate power (proportion of 1000 tests giving F-tests significant at the 0.05 level) for pairwise tests based on sets of random variables generated for coefficients of variation as given in the left margins. Power for the entries under s^2 for the lognormal distribution was checked against Pearson's (*44*) tables and showed excellent agreement. These results suggest that the two tests perform in about the same manner, regardless of the distribution. The small but consistent advantage of the "s^2" test on the gamma distribution is encouraging in terms of the practical approach of F-tests on log-transformed data. The close agreement of the two tests on lognormal data hints that the z-statistic may be approximately chi-square distributed for lognormally distributed random variables.

Scheffé's Test for Equality of Variances. In practice, the tests given above may not be very useful since one may want to intercompare a number of variances with different degrees of freedom. Bartlett's test is widely used for that purpose, although it is sensitive to deviations from normality (*45*). Scheffé (*46*) suggests an alternative approximate test, based on an analysis of variance of log-transformed variances.

Convenient power tables are given by Kastenbaum et al. (*47, 48*) and Bowman (*49*), arranged in terms of the criterion:

$$\tau = \frac{|\mu_{\max} - \mu_{\min}|}{[\mathrm{Var}(y)]^{1/2}} \qquad (14)$$

where $\mu_{\max}$ and $\mu_{\min}$ are the maximum and minimum mean values in the data, and all other means are assumed to fall midway between these two. Scheffé's approximation to the variance can be written as:

$$V(y) = \frac{2}{n-1} + \frac{k_4}{n\sigma^4} \qquad (15)$$

where k_4 is the fourth cumulant, which can be obtained from the cumulant generating function of a log-transformed random variable from a gamma distribution. Expressing the various components of Equation 14 in terms of the coefficients of variation (and retaining only first terms in approximations), we obtain an approximation to Equation 14 as:

$$\tau^* = \frac{|\log_e c_1^2 - \log_e c_2^2|}{\left[\dfrac{2}{n-1} + \dfrac{2c^2}{n}\right]^{1/2}} \qquad (16)$$

where c_1 is the larger of the coefficients of variation being compared.

As a check on the various approximations, we again resorted to simulation, using sample sizes of 21 log-transformed random variables from a simulated gamma distribution. Since Scheffé's method depends on a one-way analysis of variance of log-transformed variances, we used the minimum possible number of variances (i.e., 2) for each set and generated either 5 or 10 such pairs for each trial. The smaller coefficient of variation was set at 0.20, and the others arranged in accord with the assumptions for the power tables (i.e., one pair at each extreme and the remainder midway between). Each test was replicated 100 times, giving a comparison between simulated and tabular power (Table II).

Although our results are of insufficient scope to be broadly conclusive, they do suggest that the approximations of Equation 16 may provide a useful guide to the power of Scheffé's test, and thus provide a useful notion as to the order of differences in coefficients of variation that might be detected. If the underlying distributions are lognormal, the criterion becomes:

$$\tau = \frac{|\log_e \sigma_1^2 - \log_e \sigma_2^2|}{\left[\dfrac{2}{n-1}\right]^{1/2}} \qquad (17)$$

Discriminating Between Distributions. Our evidence thus far suggests that it may not be particularly important whether the gamma or the lognormal distribution actually holds—log transformation will apparently serve many practical purposes in either case. A natural further inquiry has to

Table I. Simulated Power for F-Tests Using s^2 and z Statistics

	Gamma distribution					Lognormal distribution			
	$n = 6$		$n = 21$			$n = 6$		$n = 21$	
c	s^2	z	s^2	z	c	s^2	z	s^2	z
0.447[a]	0.049	0.043	0.074	0.055	0.400[a]	0.046	0.047	0.041	0.043
0.500	0.091	0.077	0.143	0.123	0.450	0.070	0.074	0.111	0.117
0.577	0.150	0.141	0.355	0.309	0.600	0.179	0.174	0.494	0.486
0.707	0.300	0.253	0.696	0.659	0.700	0.274	0.255	0.701	0.699
1.00	0.607	0.543	0.978	0.971	0.800	0.341	0.323	0.815	0.812
0.200[a]	0.049	0.048	0.074	0.069	0.200[a]	0.046	0.046	0.041	0.042
0.258	0.141	0.135	0.320	0.308	0.250	0.112	0.111	0.214	0.213
0.301	0.221	0.215	0.589	0.582	0.300	0.198	0.187	0.545	0.544
0.447	0.529	0.520	0.740	0.720	0.400	0.393	0.384	0.900	0.902
0.707	0.864	0.852	0.900	0.900	0.600	0.695	0.696	0.996	0.995

[a] Entries in this block of the table are based on paired F-tests between samples generated from this coefficient of variation and all listed coefficients of variation.

Table II. Simulated and Tabulated Power for Scheffé's Test

	5 pairs of variances				10 pairs of variances		
c	Simulated power	Tabular power[a]	Tabular power[b]	c	Simulated power	Tabular power[a]	Tabular power[b]
0.200	0.04	. . .	. . .	0.200	0.04	. . .	. . .
0.408	0.61	0.65	0.61	0.447	0.59	0.73	0.68
0.447	0.70	0.76	0.72	0.500	0.79	0.85	0.80
0.500	0.79	0.86	0.82	0.577	0.92	0.95	0.91
0.577	0.91	0.95	0.92	0.707	0.95	0.99	0.98
0.707	1.00	0.99	0.98	1.000	1.00	>0.995	>0.995

[a] Using Equation 14 and retaining four terms in series approximations to the component parts. [b] Using Equation 16.

do with the prospects for actually discriminating between the two distributions. Jackson (*50, 51*) gives "separate families" tests [based on work by Cox (*52, 53*) on likelihood ratio tests] but suggests that large samples may be needed for discrimination (the tests depend on asymptotic results). Some simulation trials have persuaded us that this is indeed the case. For the range of coefficients of variation of main interest here (say less than 50%), samples of fewer than 200 observations yield unacceptably low power. For $c = 0.5$ and $n = 200$, the simulated power is about 0.80. Thus, impractically large samples are required for case-by-case testing.

Sampling

Much of this paper has necessarily been devoted to establishing a basis for designing sampling schemes. Since the systems considered are dynamic and the objectives in studying such systems are seldom simple and straightforward, we believe such a detailed background is essential for effective sampling design. Unfortunately, virtually none of the studies of contaminants in ecological systems known to us has been designed in the sense of sample survey planning. Space precludes including details, but a general basis for field sampling is suggested in the balance of this section.

Survey Sampling. When study objectives are mainly concerned with the estimation of a mean or total, the assumption of a constant coefficient of variation greatly simplifies survey design. A rationale and methods for testing for constancy of the coefficient of variation have been presented above, and Eberhardt (*54*) summarized previously observed values for a number of trace substances. Although a wide variety of techniques for sampling design are available [see, for example, the text by Cochran (*3*)], the main method for circumstances considered here seems likely to be stratified random sampling. With the assumption of a constant coefficient of variation, the formula for optimum allocation in stratified random sampling can be written as:

$$n_h = \frac{n s_h w_h}{\sum\limits_h s_h w_h} = \frac{n \bar{x}_h w_h}{\sum\limits_h \bar{x}_h w_h} \qquad (18)$$

where w_h pertains to proportion of total area in the hth stratum, $\bar{x}_h$ denotes a stratum mean, and n is the total sample to be allocated.

If the finite population correction can be neglected, total sample size determination can be accomplished in terms of standard errors relative to the mean, which reduces to:

$$\frac{s}{\bar{x}\sqrt{n}} = \frac{c}{\sqrt{n}}$$

thus avoiding the need for an advance estimate of the population mean.

Our arguments for logarithmic transformations given in the preceding section permit a convenient expression of population means for power calculations. Since the arrangement for calculation of minimal power involves the *difference* between a maximum and minimum value after a logarithmic transformation, the original (untransformed) values can be expressed as a *ratio*. One can thus again conveniently proceed without specifying means.

Another important tool in field sampling is "double sampling" (cf., Chap. 12 of ref. *3*) in which a relatively inexpensive type of measurement is used in conjunction with some expensive chemical analysis. In a sense, the costly but accurate method serves to "calibrate" a large sample in which the less expensive method is used. We have investigated the technique for combining rather expensive "wet chemistry" analyses for plutonium with much cheaper determinations with field or laboratory detection instruments *(55)*. A particularly important application in surveys of biota for contaminants is in the use of body weights of individual animals as an auxiliary variable in double sampling, based on Equation 9 above. The cost differential between simply weighing, say, a fish and doing an analysis for DDT or PCB's makes such a procedure extremely attractive. An analysis of such data (DDT, PCB's, and mercury) using weights and lengths of fish has been given by Eberhardt *(56)*.

Analytical Sampling. In circumstances where survey objectives have to do with establishment of a baseline and monitoring for change, the use of auxiliary variables such as body weight again offers some obvious advantages. In this case, the statistical analysis may include both hypothesis testing and estimation and is most conveniently done with regression techniques in an analysis of covariance. Frequently time may also serve as an important auxiliary variable, as illustrated in the simple retention or "decay" model:

$$y = y_0 e^{-\mu t} \tag{19}$$

which expresses the concentration (or burden) of some substance lost at a constant rate (μ), starting with an initial quantity (y_0) at $t = 0$. As discussed previously in this paper, this simple model will best be treated by logarithmic transformation, giving:

$$\log_e y = \log_e y_0 - \mu t \tag{20}$$

and for use of body weights with Equation 9 above:

$$\log_e y = \log_e \alpha - \beta \log_e w \tag{21}$$

Intercepts in the equations are thus estimated in logarithms. Attempts to estimate the intercepts by transformations like $\hat{\alpha} = \exp(\widehat{\log_e \alpha})$ result in biased estimates. Finney *(57)* gave a result that may be used for an improved estimate, and Heien *(58)* has done some recent work on the problem, while Bradu and Mundlak *(59)* treat some more complicated relationships.

The possible use of time (t) as a concomitant variable is nicely illustrated by data of the kind reported by Turner *(60)*, Martin *(61)*, and Martin and Turner *(62)*. These authors report some studies of radioactive materials produced in testing of a nuclear device (the "Sedan" test). In this case, the local fallout from the test was apparently deposited in a very short span of time, so that Equation 19 serves as a suitable model for retention of fallout materials by plants, and an analysis of covariance thus can be used to study differences in areas, species, etc., "adjusted" for time, as well as to compare loss from place to place and so on.

A similar application for the retention of DDT by plants and animals is possible in the study conducted by Meeks and Peterle *(63)*. In an attempt to model the data *(12)*, it was necessary to use two "compartments" to represent retention of DDT by plants. One of these compartments evidently had a short retention time; therefore, after sufficient time had elapsed, the loss rate for the second compartment might be studied by regression methods.

Sampling for changes (monitoring) brings in additional questions, some of which have been discussed by Eberhardt *(54)*. Rather than estimating a total or mean, one may prefer to attempt to create a *map* of concentrations, as has been done for airborne contaminants *(64)*. A detailed methodology for this purpose has been developed in economic geology *(65)*. Space precludes discussion here, but there is an evident need to adapt these methods in the contexts of this paper.

When more complex models are required, an efficient design for sampling in the field or laboratory may call for a complex mathematical analysis and for data fitting by nonlinear least-squares methods. Box and Lucas *(66)* have proposed a method for selecting trial values of experimental variables (e.g., temperature, pressure, time of observation, etc.) so as to minimize the "confidence ellipsoid" for parameter estimates. In its general form, the scheme permits study of a multivariate system, but our immediate interest here is in the univariate case, where a dependent variable, such as concentration of a trace substance, is functionally related to time through a well-defined model. The method requires advance estimates of parameter values and yields a set of times at which observations should be taken to minimize the joint confidence set for adjusted parameter estimates. The set of times is selected so that the determinant $|(\mathbf{F'F})^{-1}|$ is made as small as possible, where $\mathbf{F}$ is a matrix of partial derivatives of the function, taken with respect to each parameter (columns of the matrix) and evaluated at the sampling times (rows of the matrix). Just how to select the times so that the determinant is minimized is not specified by the method, and Box and Lucas restrict the number of sampling times (n) to equal the number of parameters (p) in the model.

Our experience with the method has thus far been limited to exploration of some of the operational problems associated with its use. Recent reports *(67–70)* indicate that optimal schemes employing more sampling points than there are parameters to estimate will often simply constitute replications of the basic set of points in which $n = p$. Such schemes do not, of course, offer anything in the way of protection against choice of the wrong model. In many cases, it will be desirable to have additional sampling points in consequence of uncertainty as to accuracy of the initial parameter estimates. As we have noted, replication is desirable as a means of testing constancy of the coefficient of variation, and replicates will also be wanted to provide independent variance estimates for appraising "fit" of a model. Note that the "Box and Lucas" scheme is not equivalent to response surface methodology, although there are certain similarities. A recent useful review is that of Cochran *(71)* who gives many useful references, including designs for testing models.

The literature dealing with the optimum sampling scheme described above is set largely in an experimental context (mostly industrial research), wherein independence of observations may be secured by repeated runs of the experiment. In actual studies of contaminants in natural settings, replicates will often be available only as independently selected samples of the same kind (e.g., same species) taken at the same time. Field sampling plans will thus need to be designed to achieve the same kind of independence (zero covariances) insofar as possible.

Where analytical costs are substantial, there is a natural temptation to pool a number of individuals (animals, for example) into a single sample, thus both reducing costs and hopefully tending to normalize the distribution of sample values. We suggest, however, that it would be well to consider the implications of our previous discussion of the statistic z before deciding on such a course. Similarly, if body burden is related to weight as in Equation 9, pooling animals of different weights introduces complications.

As a general rule, additional samples taken at fixed points in time can be expected to cost less than will the same total number of samples spread over more times. This is because most field operations will have certain costs associated with preparing for a field trip and traveling to the sampling area. Consequently, it should be worthwhile to attempt to produce cost functions that consider the more or less fixed costs, travel time, time and material, cost of sampling, and so on. Another area of investigation that seems worth additional study is the examination of residuals about fitted curves in the hope that the behavior of such residuals may shed some light on the validity of the assumed model.

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Determination of Vinyl Chloride at μg/l. Level in Water by Gas Chromatography

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■ A quantitative method for the determination of vinyl chloride in water is presented. An inert gas is bubbled through the water sample to transfer the vinyl chloride to the gas phase. The vinyl chloride is concentrated on silica gel or Carbosieve-B under noncryogenic conditions and determined by gas chromatography with a halogen-specific detector. The method is tested over a range of 4–40 μg/l. Based on earlier work with similar compounds, a useful working range of 0.1–2500 μg/l. should be achievable. Gas chromatography–mass spectrometry methods for providing confirmatory identification of vinyl chloride are described.

Current reports (*1*) describing the chronic effects of airborne vinyl chloride on industrial workers have triggered widespread interest in monitoring other environmental carriers that may ultimately affect the health of man. Our aqueous environment is the second most likely medium for man's involuntary contact with vinyl chloride. Wastewaters and sediments from diverse vinyl chloride manufacturing processes contain varying amounts of vinyl chloride. Products constructed from virgin polyvinyl chloride outgas vinyl chloride; therefore, home water systems and municipal water supplies using polyvinyl chloride plumbing are likely to contain trace amounts of this hazardous compound. Vinyl chloride has, until recently, been used as a propellant for aerosol cans; thus, there is the possibility of long-term contamination of groundwaters in the vicinity of sanitary landfills. For these reasons, the Environmental Monitoring and Support Laboratory (EMSL) has investigated methodology for the detection and analysis of trace amounts of vinyl chloride in the aqueous environment.

Direct aqueous injection gas chromatography using flame ionization, microcoulometry, electrolytic conductivity, and mass spectrometry for detection has been used for the identification and measurement of many common waterborne pollutants (*2–5*). These techniques were applied to the determination of vinyl chloride in industrial effluents (*6*). The reported lower limits of detection vary, but 100 μg/l. appears to be conservative for vinyl chloride using a flame ionization detector. Halogen-specific detectors, for example, the microcoulometric and electrolytic conductivity, are less sensitive (approximately 1000 μg/l.). However, they do improve the qualitative accuracy of the determination.

A method for liquid-liquid extraction of vinyl chloride from aqueous solution has also been reported (*6*). As much as 500 ml of water is extracted with 1 ml of carbon tetrachloride. One microliter of the extract is analyzed by gas chromatography. The reported lower limit of detection is approximately 0.1 μg/l. Extraction efficiencies for vinyl chloride are reported to be about 77% at 1–10 μg/l. and near 100% at 0.2–3 mg/l.

Bellar and Lichtenberg (*7*) reported a method for the analysis of purgable volatile organics contained in aqueous solution at the sub-μg/l. level. The work presented here represents a specific application of this method to the determination of one very significant environmental pollutant, vinyl chloride.

Experimental

Apparatus. A Perkin-Elmer 900 gas chromatograph was equipped with a dual-flame ionization detector, a microcoulometric detector (halide mode), and a Hall electrolytic conductivity detector (halide mode). Dual stainless steel columns, 180 cm (6 ft) long × 2.67 mm (0.105 in.) i.d., were packed with Chromosorb-101 (60/80 mesh). The oven temperature was isothermal at 90 °C or programmed from 90 to 200 °C at 10 °C/min. Nitrogen, at 60 ml/min, was employed as the carrier gas. Desorber #1 (Figure 3) was used with this instrument.

A Varian Aerograph 1400 gas chromatograph with a Finnigan 1015C quadrupole mass spectrometer controlled by a System Industries 150 data acquisition system was employed. The glass column, 240 cm (8 ft) long × 2 mm (0.078 in.) i.d., was packed with Chromosorb-101 (50/60 mesh). Helium, at 30 ml/min, was employed as the carrier gas. The initial oven temperature of 90 °C was held for 3 min and then programmed to 220 °C at 4 °C/min. Desorber #2 (Figure 4) was used with this instrument.

The purging device, trap, and desorption system shown in Figures 1–4 represent improvements in design over those reported in the original work (*7*).

Reagents. Water that is free of interfering organics was prepared by passing distilled water through a Millipore Super-Q water treatment system.

Standard solutions of vinyl chloride were prepared as follows: Approximately 8 ml of acetone was placed into a 10-ml volumetric flask. The flask and contents were carefully weighed. Vinyl chloride was slowly bubbled into the acetone from a finely drawn glass tube for about 2 min. The flask and contents were reweighed, diluted to volume, and stoppered. The weight gain, 50–200 mg, was used to calculate the concentration. A secondary dilution of 10 ng/μl of vinyl chloride in acetone was prepared from this standard. These standard solutions, when stoppered and stored at 4 °C, were stable for at least 1 week.

Procedure. *Trap Conditioning.* Newly packed traps were conditioned at approximately 200 °C with a nitrogen backflush flow of 20 ml/min for 16–24 h with one of the desorbers vented to the room. Each day before use, traps were placed into the desorber and conditioned at 150 °C for approximately 10 min while being backflushed with nitrogen at 20 ml/min.

Purging and Trapping. Unless otherwise stated, samples were purged and trapped as follows: With nitrogen flowing through the purging device (Figure 1) at 20 ml/min, the trap inlet (Figure 2) was attached to the purging device exit using a removable compression fitting. The trap vent was inserted into the exit end of the trap. Five milliliters of sample was injected into the purging device using a 5-ml syringe. After purging the sample for 10 min, the trap was removed from the purging device, and the trap vent was removed from the exit end of the trap. All samples were analyzed within 10 min of trapping.

Desorption and Analysis. *Desorber #1 (Figure 3).* The gas chromatographic oven was cooled below 30 °C with the oven door open. After removing the plug from the desorber, the trap was inserted into the desorber. The trap backflush flow fitting was then locked into place on the trap exit. In this manner the

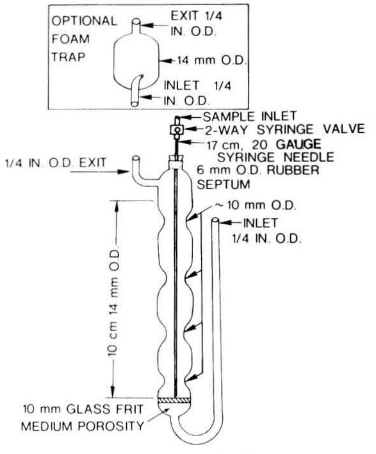

Figure 1. Purging device

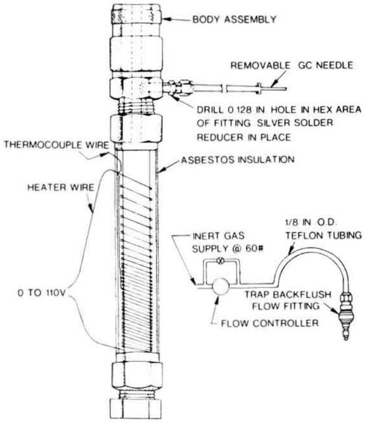

Figure 4. Desorber #2

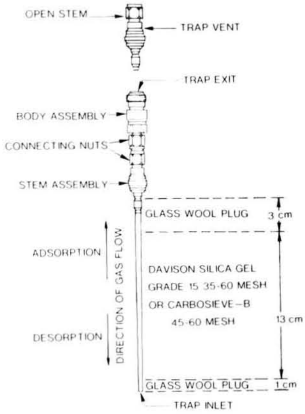

Figure 2. Trap

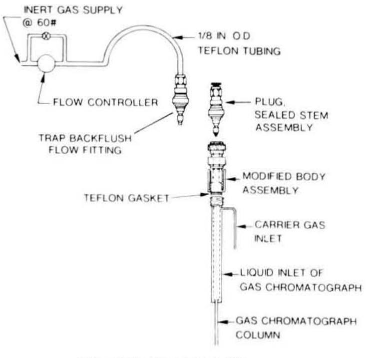

Figure 3. Desorber #1

trap was backflushed with nitrogen at 20 ml/min for 4 min at 150 °C. Then the trap backflush flow fitting was removed (trap still locked into place), the oven lid closed, and the oven rapidly heated to its normal or initial operating temperature. Gas chromatographic analyses were carried out under these conditions.

After analysis, the trap was removed by: inserting the trap vent into the trap exit fitting (to vent inlet system), removing the trap, resealing the gas chromatographic (GC) inlet system with "the plug", removing the trap vent, and resealing the trap inlet with a removable compression fitting cap.

Desorber #2 (*Figure 4*). The gas chromatographic oven was cooled to below 30 °C with the oven door open. The needle was inserted into the liquid inlet system on the gas chromatograph. The trap was then inserted into the desorber and locked into place. The trap backflush flow fitting was locked into the trap exit flow fitting. The trap was then backflushed with nitrogen at 20 ml/min for 3 min at 150 °C. After 3 min the needle was removed from the liquid inlet system, the oven lid closed, and the oven rapidly heated to the normal or initial operating temperature. Gas chromatographic analyses were performed under these conditions. After sample transfer, the trap was removed from the desorber and sealed for future use.

Quantitative Measurements. All quantitative data presented in this paper were obtained with a trap packed with silica gel, the Perkin-Elmer 900 gas chromatograph, and a halogen-specific detector.

Investigation of Method Variables. Initial studies were carried out to determine what volume of water-saturated purge gas can pass through the trap packed with various adsorbants before vinyl chloride is vented. The purge volume of nitrogen needed to quantitatively transfer vinyl chloride from the aqueous phase to the gaseous phase was also determined. The purging device was charged with 5.0 ml of organic-free water containing approximately 50 ng of vinyl chloride. The trap, packed with 13 cm of Chromosorb-103, Carbosieve-B, or silica gel (Grade 15), was attached to the exit of the purging device. A known amount of nitrogen was passed through the purging device and trap, and the desorbed vinyl chloride was quantitatively determined. The experiment was repeated with each adsorbant using progressively larger purge volumes. The data collected show Carbosieve-B and silica gel to give quantitative recovery with purge volumes from 150 to 400 ml at 20 ml/min (Figure 5). The 400-ml purge volume is more than 100% greater than that required for quantitative transfer of vinyl chloride. Chromosorb-103 and presumably other porous polymers are not suitable for trapping vinyl chloride.

To determine the effect of sample collection and storage on the accuracy of the method, 1 l. of Ohio River water contained in a 1-l. separatory funnel was dosed with vinyl chloride at 20 μg/l. This mixture was then used to fill several 50-ml, glass-stoppered bottles. Care was taken so that no air passed through the sample as the bottles were filled. The bottles were over-filled, and part of the sample was displaced with the ground-glass stopper so that no headspace was trapped in the

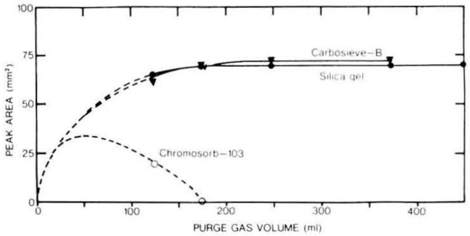

Figure 5. Purging and trapping efficiency of vinyl chloride from water using various sorbents

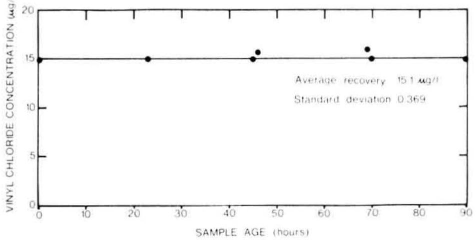

Figure 6. Recovery of vinyl chloride from dosed Ohio River water stored in glass-stoppered bottles with zero headspace at ambient temperature

bottle. The bottles were then stored in a laboratory hood under ambient conditions. Seven of the samples, having no headspace, were randomly selected and analyzed over a period of 93 h. The data show that the recoveries were constant over the period of study (Figure 6). The average recovery was 15.1 ± 0.4 μg/l. The initial 25% loss is attributed to the headspace above the dosed sample while it was contained in the separatory funnel. Losses due to headspace or exposure to the atmosphere are further illustrated below.

The time zero sample from the above experiment, now containing 5 ml of headspace, was reanalyzed at 15 min and again at four additional times over a period of 300 min (Figure 7). Each time 5 ml of sample was withdrawn, leaving an additional 5 ml of headspace. Care was taken not to agitate the sample during the storage period. The results show that as the headspace increases, the recovery of vinyl chloride decreases. The total loss over the time period was about 50% or about 10%/h.

The loss of vinyl chloride from water in an open narrow neck container at ambient temperature was observed by dosing 50 ml of tap water in a 50-ml volumetric flask with 10 mg/l. of vinyl chloride and 20 mg/l. chlorobenzene. Chlorobenzene is relatively nonvolatile and was used as an internal standard. These analyses were done by direct aqueous injection gas chromatography, not by the purge and trap technique. The recovery of vinyl chloride relative to the chlorobenzene is shown in Figure 8. The loss of vinyl chloride was linear throughout the time period with a total loss of 35% or about 17%/h. The recovery of chlorobenzene was constant throughout the study.

To test the procedure over a wide concentration range, a standard curve was prepared by injecting known amounts of a 10 ng/μl vinyl chloride in acetone solution into the purging device containing 5.0 ml of organic-free water. Each mixture was then purged and analyzed. The response obtained by microcoulometric titration (MCT) gas chromatography was linear over a concentration range of 4–40 μg/l. (Figure 9). Based on data collected for similar halogenated hydrocarbons, the method may be useful up to 2500 μg/l.

Gas chromatography-mass spectrometry (GC/MS) techniques were tested with this method to determine their compatibility and usefulness as a qualitative confirmation technique for vinyl chloride at μg/l. concentrations. Organic-free water dosed with 50 μg/l. of vinyl chloride was analyzed according to the purge and trap procedure. Figure 10 represents the GC/MS total ion current profile of vinyl chloride recovered from this water. The x-axis labeled "spectrum number" is equivalent to the time axis on a normal gas chromatogram. The vinyl chloride peak was eluted as the mass spectrometer scanned over spectrum numbers 129–136. The other peaks appearing at spectrum numbers less than 100 are due to H_2O, CO_2, and general interferences. These peaks always occur but in no way interfere with vinyl chloride or other substituted hydrocarbons.

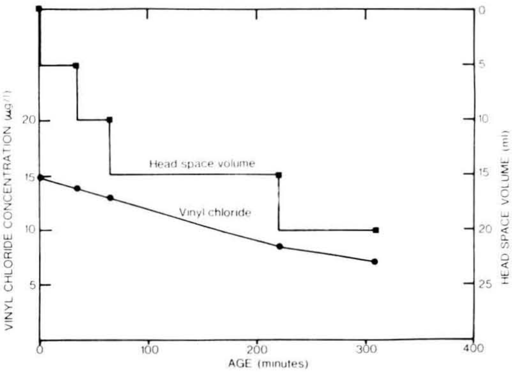

Figure 7. Recovery of vinyl chloride from dosed Ohio River water stored with variable headspace at ambient temperature

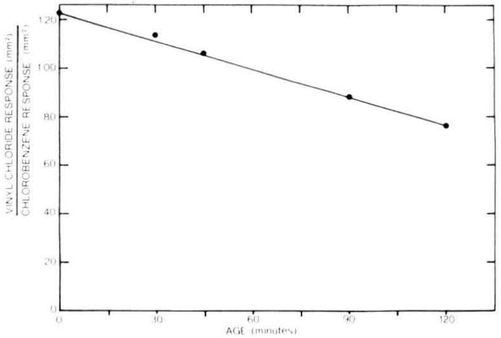

Figure 8. Recovery of vinyl chloride from dosed tap water stored unstoppered at ambient temperature

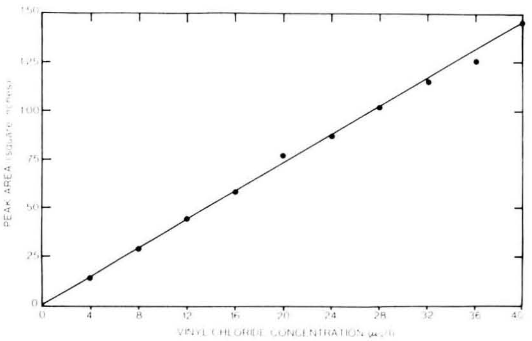

Figure 9. Response curve for vinyl chloride using microcoulometric detector

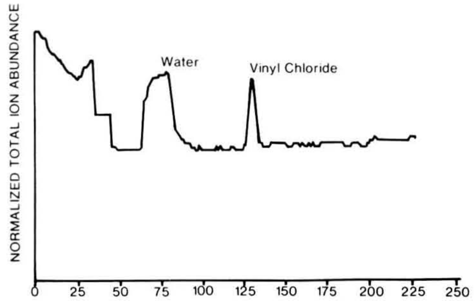

Figure 10. Total ion current profile of vinyl chloride recovered from water

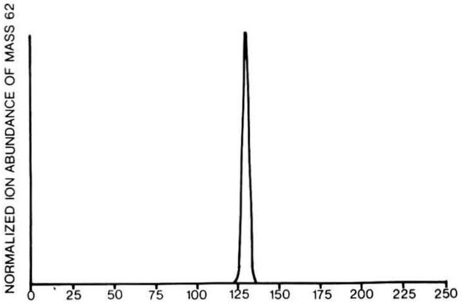

Figure 12. Selected ion current profile of mass 62 for vinyl chloride

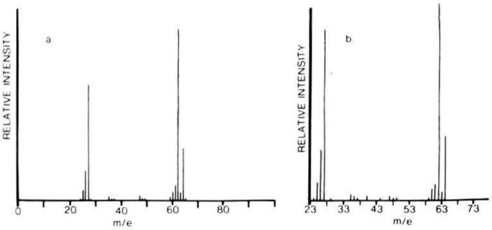

Figure 11. a. File mass spectrum of vinyl chloride (chloroethylene). b. Mass spectrum of sample

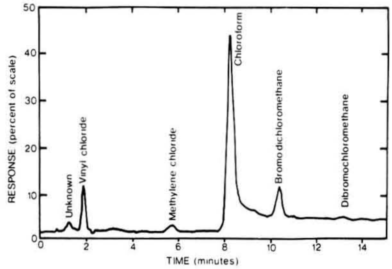

Figure 13. Microcoulometric gas chromatogram of organohalides recovered from tap water dosed with vinyl chloride (sensitivity 150 ohms)

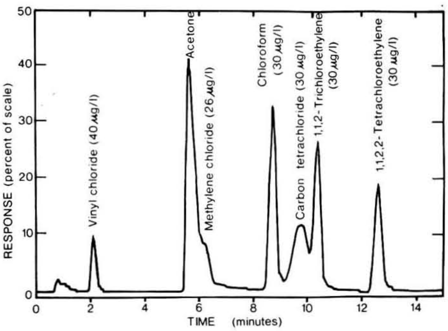

Figure 14. Electrolytic conductivity gas chromatogram of organohalides recovered from dosed seawater (full-scale response, 160 μmhos)

Figure 11 shows the mass spectrum obtained by subtracting each mass-to-charge ratio (*m/e*) response obtained in spectrum 123 from the corresponding *m/e* response in spectrum 128. In this manner, normal instrument noise and background (spectrum 123) are minimized, providing a mass spectrum of gas chromatographic effluent occurring at spectrum 128. Comparing mass spectrum 128 with background subtracted gives a positive match to the file mass spectrum for vinyl chloride (*9*). Close examination of the vinyl chloride mass spectrum shows a relatively high abundance of an ion with a *m/e* of 62 (the molecular ion). The work of McLafferty (*10*) shows that this ion is characteristic of vinyl chloride. Other reported compounds producing abundant *m/e* 62 ions are easily resolved from vinyl chloride using the gas chromatographic conditions described in this paper. With this in mind, the computer was reprogrammed to scan the data and construct a selected ion current profile consisting of peaks that produce a *m/e* 62 ion (Figure 12). The usefulness of this technique, when only vinyl chloride data are desired, becomes evident when Figure 12 is compared to Figure 10.

Figure 13 represents a typical gas chromatogram obtained from chlorinated tap water which has been dosed with vinyl chloride. The chloroform, bromodichloromethane, and dibromochloromethane are common to chlorinated drinking waters and result from the chlorination process (*8*). Low levels of methylene chloride are often observed in samples analyzed by this technique. These are attributed to method background. Figure 14 represents the chromatogram obtained from a seawater sample dosed with vinyl chloride and other organohalides. Using the Hall electrolytic conductivity detector, response was obtained for the acetone used to prepare the vinyl chloride standard solution.

Smith and Ohlson (*11*) have reported on the interaction between olefins in the gas phase and cations such as Ag^+. If such interactions were to occur under the conditions used for purging vinyl chloride from water, a negative interference would result. To determine whether or not this does occur, dilute solutions of Ag^+ and Cu^+ were added to distilled water samples dosed with vinyl chloride. The samples were purged and analyzed according to the procedure described above. No effect on the recovery of vinyl chloride was observed. With these results and those obtained on seawater, we concluded that the presence of cations is not likely to interfere with the determination of vinyl chloride in water.

Conclusions

The purge and trap technique (*7*) has been modified and applied to the determination of vinyl chloride in sea, river, tap, and distilled water. Optimum conditions for the recovery of vinyl chloride are as follows: the adsorbent trap of 13.0 cm of Davison grade 15 silica gel (35/60 mesh) or Carbosieve-B (45/60 mesh) with a sample purge time of 10 min at 20 ml/min nitrogen and a trap desorbing temperature of 150 °C. A halide-specific detector (MCT or conductivity) is used.

Detection levels from 4 to 40 μg/l. have been studied. It is expected that the useful range can be extended to 2500 μg/l. Standard GC/MS techniques can be employed to obtain unequivocal identification of vinyl chloride. Samples containing vinyl chloride can be stored at least four days in completely filled, glass-stoppered bottles without significant losses. Losses between 10 and 20%/h can be expected from unconfined samples or samples containing a sealed headspace.

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NOTES

Determination of Micro-Quantities of Chrysotile Asbestos by Dye Adsorption

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■ A method of analysis for airborne asbestos is developed by a differential dye adsorption technique. Estimation of quantities of chrysotile asbestos is possible down to the 100-μg level and requires only a differential-reading spectrophotometer. This method is also applicable to crocidolite. For applications in industrial areas where chrysotile asbestos constitutes over 95% of the asbestos used in this country, the asbestos samples must first be separated from interfering minerals by a density flotation process.

The development of a density gradient method for separating asbestos from minerals that interfere with its analysis (*1*), on the basis of research carried out in our laboratories, opened up new possibilities for quantitative estimation of isolated asbestos. Bagioni (*1*) applied an infrared method which was sensitive to fractions of a milligram and could differentiate chrysotile (carcinogenic) from amphibole types of asbestos. The present research describes a method based on adsorption of the ammonium salt of aurin tricarboxylic acid which facilitates estimation of chrysotile asbestos with sensitivity down to the 100-μg range and requires only a good spectrophotometer for application. This method constitutes a significant improvement over expensive and time-consuming analysis by electron microscopy for monitoring dangerous forms of asbestos in ambient air.

The density gradient method of separating chrysotile asbestos from interfering minerals can cause difficulties in subsequent infrared analysis in that residues of the 1,1,2,2-tetrabromoethane used in the gravity flotation process may also absorb around 2.72 μ which is the wavelength used for identifying chrysotile asbestos. Therefore, it is imperative that complete removal of the difficultly volatile 1,1,2,2-tetrabromoethane is accomplished for accurate infrared analysis. Our quantitative dye technique is not affected by such residues of solvent nor of serpentine, since a different spectral region is used.

The applications of a dye adsorption method of analysis are quite valuable in detecting one of the most common forms of asbestos, chrysotile, above allowable limits for both industry and ambient air samples. Present electron microscopy and x-ray methods of analysis are dependent on the structure of the asbestos and employ costly and time-consuming methods that curtail regular monitoring of such areas. Proper control of asbestos as a pollutant is dependent on its detection, and the method outlined below is one that is readily applicable, inexpensive, and easy to use.

Experimental

Preliminary search for a dye that would be selective for asbestos and whose decrease in absorbance would be sensitive enough for detection in a spectrophotometer resulted in the selection of Aluminon which dyed several types of asbestos a purple-rose color. Most dyes tested were pH dependent, and a range from 4.5 to 5.0 gave optimum adsorption of Aluminon on asbestos. The buffer solution used was prepared from potassium hydrogen phthalate and sodium hydroxide as directed in the "Handbook of Chemistry and Physics" and did not interfere with the analysis. The concentration of dye that would be sure to saturate 1 mg of asbestos was found by using 1 mg of chrysotile asbestos in varying concentrations of the dye and then measuring differences in absorbancy of the supernatant and the original dye solution. A concentration of 0.1 g dye per 500 ml of buffer solution was used and assured maximum adsorption on amounts of asbestos less than 1 mg. Types of asbestos tested, other than chrysotile and amphibole, were supplied by Raybestos Co., Stratford, Conn.

The procedure for the routine analysis by this method consists of suspending the asbestos residue in 3.5 ml of the prepared dye solution and heating in a beaker of water at 50–60 °C for 1 h until the asbestos fibers swell and are dyed a purple-rose color. It is then centrifuged, and the supernatant is pipetted off. Necessary water is added to the supernatant to replace that which has evaporated. The supernatant is then read at 525 nm on the DK-2 spectrophotometer vs. a reference of the original dye solution. A scale of 0–200% transmittance was used. With amounts of asbestos less than 1 mg, more sensitive scale expansions can be used on the spectrophotometer allowing detection to 100 μ or less. If a spectrophotometer is not available with such sensitive scale expansions, a cell with a smaller path length would suffice and give equal detection limits. The resulting readings can be plotted vs. the amount of asbestos used to construct a calibration curve to be used for unknown amounts of chrysotile asbestos samples. This graph relates decreases in adsorption to micrograms of asbestos (Figure 1).

Results and Discussion

Heating is important to the dye adsorption to obtain reproducible results and tends to physically alter the asbestos fibers so as to increase the adsorption rate. The graph in Figure 1 relates the amount of asbestos to the percent decrease in transmittance of dye and can easily be used as a calibration curve for further quantitative estimations.

Different types of asbestos were used as samples for this dye adsorption method, and both chrysotile and crocidolite forms gave good adsorption data. Amphibole and amosite asbestos did not adsorb the dye to any significant amount, and antrophyllite asbestos had minimal dye adsorption levels. Since chrysotile asbestos is the principal variety of asbestos used in industry, larger than 95%, this method would be valuable due to chrysotile's consistent and high adsorption data (*2*). The surface area of the asbestos fiber would also be related to its adsorption of dye and possibly to the carcinogenicity of the inhaled fibers. Independent surface area measurements were not taken, but such an investigation might yield interesting data.

The dye adsorption method presented here would lend itself readily to monitoring air on the premises of manufacturing processes using asbestos, where asbestos emission to ambient air may not exceed 25 $\mu g/m^3$.

To meet general ambient air quality standards of 30 ng/m^3, it would be helpful to have a method with still greater sensitivity (*3*). The dye adsorption method should be readily adaptable to adsorption of a fluorescent substance which might offer this possibility. However, several dichlorofluorescein dyes have been tried, and a reproducible method has not yet been perfected.

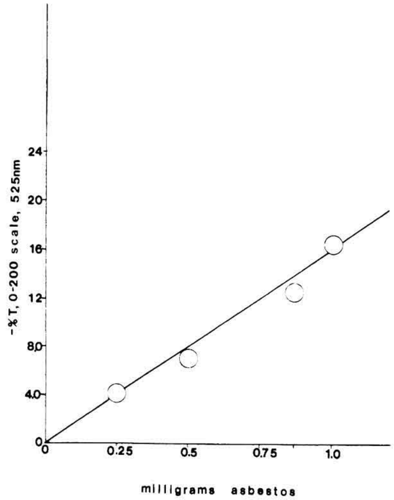

Figure 1. Relationship between amounts of chrysotile asbestos and percent decrease in transmission at 525 nm of Aluminon dye (0.1 g/500 ml) due to adsorption on surface of asbestos fibers

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Capture of Hg^{2+} Ions from Effluent Stream by Cellulose Derivatives

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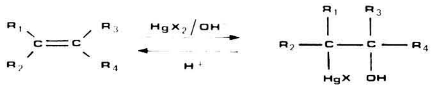
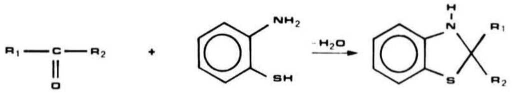
■ The ability of cellulose derivatives with 10-undecylenic acid supported on celyte and with *o*-aminothiophenol to capture Hg^{2+} ions from aqueous solutions is tested. These systems are useful tools for removal of Hg^{2+} ions from low concentration (0.5 mg Hg/ml 10^{-3}) aqueous solutions and can lower them to a safe concentration of about 0.05 mg Hg/ml 10^{-3}. A practical operational scheme is proposed which involves the sequential elution of a Hg^{2+}-containing solution through a column filled with cellulose 10-undecylenate support followed by elution through a column filled with *o*-aminothiophenol cellulose derivative.

Methyl mercury and homologous short chain compounds exhibit effects in man which differ from those effects produced by other mercury-containing compounds. These phenomena involve the nervous system with loss in limb sensitivity, gait coordination, sight, and hair (*1*). Mercury removal from water may be achieved by precipitation with sulfide (*2*), by use of ion exchange (*3–6*), by reduction and separation with metallic mercury (*7*), and by sorption on protein such as wool (*8*) or on nitrogen-containing chemically modified cellulose (*9*).

The system reported here is based on the use of cellulose derivatives functionalized with alkenes. These substrates were selected because of low reagent price and reaction reversibility which allows mercury recovery and subsequent possible substrate neutralization in the purification cycle. Mercury salts form adducts with alkenes in rather mild conditions according to the following reaction (*10*):



This reaction is reversible, relatively fast, and quantitative at low mercury salt concentration (*11*). The final adduct can be readily decomposed by acids, leading to the recovery of mercury and of the corresponding alkene. With this reaction it is possible to capture, in a reversible mode, Hg^{2+} ions from an aqueous solution using alkenes anchored on insoluble supports. In addition, the condensation of an aldehyde or a ketone with 2-aminobenzenethiol normally leads to the formation of a benzothiazoline as the main product (*12*):



Reactions of these benzothiazoline derivatives with zinc, cadmium, and mercury are known (*13*). Cellulose contains a number of carbonyl groups which react with *o*-aminothiophenol to give a condensation compound, displaying a very strong affinity toward mercury ions. The reaction is carried out under mild conditions and is reproducible.

Experimental

Mercury Determination. *Spectrophotometric Method.* Mercury ions have been determined after complexation with potassium isothiocyanate, measuring the absorbance value at 281 mμ of the resulting complex $Hg(CNS)_4^{2-}$ with a Unicam/SP-800 UV/VIS spectrophotometer as previously described by Snell and Snell (*14*).

MAS-50 Method. Sample analyses have been carried out following the MAS-50-IA base method (Coleman data sheet T-243 A).

Preparation of Cellulose 10-Undecylenate Ester. A solution of 55 g of 10-undecylenic acid chloride in 200 ml of toluene was slowly added to 14 g of microcrystalline cellulose swelled in 20 ml of toluene and 70 ml of anhydrous pyridine and was refluxed for 1 h. The solvents were stripped off under reduced pressure. The obtained crude product was washed several times with water, methanol, and ethyl ether and then dissolved in benzene and precipitated with methanol. The precipitate was filtered, washed with ethyl ether, and dried under vacuum.

Support Preparation. In a typical preparation, 10 g of cellulose 10-undecylenate ester was added to 90 g of celyte suspended in acetone. The mixture was homogenized with a rotary evaporator, dried, and further homogenized. To remove all iron salts, the celyte was previously repeatedly washed with hydrogen chloride and then with water, until a neutral reaction was reached, and was finally dried at high temperature.

Preparation of Cellulose *o*-Aminothiophenol Derivative. An excess of *o*-aminothiophenol in ethanol was added to microcrystalline cellulose swelled in ethanol and was refluxed for about 2 h. The mixture was allowed to cool, and the solid was filtered, washed with ethanol and ethyl ether, and then dried.

Determination of Hg^{2+} Adsorption in Solution by Elution Method. A solution of $(CH_3COO)_2Hg$ (0.1025 g/l.) was passed through a column filled with celyte 10% cellulose 10-undecylenate ester support (55 g). The determination of the Hg^{2+} ions not retained by the support during the elution was made by the spectrophotometric method and the MAS-50 method. These results were compared with those obtained by passing the same $(CH_3COO)_2Hg$ solution through an identical column containing the same amount of celyte. The obtained results are shown in Figure 1.

Determination of Adsorption Isotherm of Celyte Cellulose 10-Undecylenate Support ("Progressive Batch Method"). Celyte (1.00 g) containing 33% cellulose 10-undecylenate was suspended in 100 ml of aqueous KOH (pH = 12) in a controlled temperature apparatus (30 ± 0.1 °C). A solution of $(CH_3COO)_2Hg$ (0.299 g/l.) was then added in 1-ml portions. After each addition the support-mercury salt mixture was magnetically stirred at a controlled temperature. Every 5 min a 1-ml sample of filtered solution was collected, and the concentration of the Hg^{2+} free ions (mg/ml per total solution) was determined by the spectrophotometric or MAS-50 method. The system was assumed to be at equilibrium when any difference in Hg^{2+} concentration was detected in two successive samples. This condition was obtained after a two-sample examination. The system can surely be considered at equilibrium after 30 min when the sample for the adsorption isotherm determination is collected. The amount of mercury anchored on the support (Hg mg/g support) was then calculated, and the results are shown in Figure 2.

Recovery of Mercury from Cellulose 10-Undecylenate Support. The mercury-saturated column was eluted with a 0.01 M HCl solution until a negative spectrophotometric

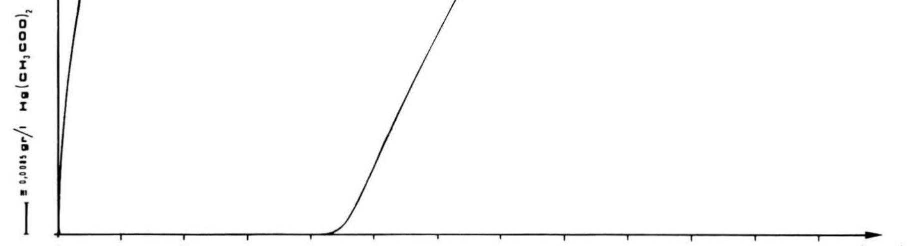


Figure 1. Elution of aqueous solution of $(CH_3COO)_2Hg$ (a) down column of celyte and (b) down column of celyte containing 10% cellulose 10-undecylenate

mercury test was obtained. The total amount of hydrogen chloride used for the recovery was excessive in terms of the potential active centers present in the support. The mercury recovery process was achieved with a simple and fast elution of the column with the hydrogen chloride solution.

On the same support, further adsorption of Hg^{2+} ions was possible after neutralization with a dilute sodium hydroxide solution and washing with water until a neutral reaction was achieved.

Determination of Adsorption Isotherm of Cellulose *o*-Aminothiophenol Derivative ("Progressive Batch Method"). An aqueous solution (100 ml) of $(CH_3COO)_2Hg$ (0.0176 g/l.) was added in a controlled temperature apparatus (20 ± 0.1 °C) to 1.00 g of cellulose *o*-aminothiophenol derivative. An aqueous solution of $(CH_3COO)_2Hg$ (0.292 g/l.) was then added in 1-ml portions. After each addition the cellulose derivative–mercury salt mixture was magnetically stirred. The Hg^{2+} free ions were determined with the same procedure used for the celyte cellulose 10-undecylenate support. The results in terms of the amount of mercury anchored (Hg mg/ml support) to the support are shown in Figure 3.

Results and Discussion

The ability of a cellulose ester with 10-undecylenic acid supported on celyte to capture Hg^{2+} ions from aqueous solutions of $(CH_3COO)_2Hg$ has been tested using an elution method. The Hg^{2+} ion concentrations in the effluent solution are reported in Figure 1 as a function of the eluent volume.

The effect of the cellulose 10-undecylenate ester in this system is seen when the results obtained with this derivative supported on celyte are compared with those obtained with a column filled with celyte only. Figure 1 shows that a celyte column is saturated after the addition of nearly 1 l. of $(CH_3COO)_2Hg$ (0.1025 g/l.), whereas a column of cellulose 10-undecylenate ester supported on the same amount of celyte reaches saturation only after the addition of 11 l. of a mercury solution of the same concentration. Under our experimental conditions, 55 g of celyte with 10% cellulose 10-undecylenate ester was able to capture 15 g of mercury. The captured mercury can be easily removed from the support (washed with a 0.01 M HCl solution) as a mercury chloride species. The regenerated support was able to capture mercury ions. The adsorption isotherm for this process is shown in Figure 2.

The adsorption isotherm for an analogous system employing the condensation product of cellulose and *o*-aminothiophenol is shown in Figure 3.

The most important difference between the two systems is that the mercury cannot be recovered as a mercury chloride species, once captured by the cellulose *o*-aminothiophenol derivative. This trend probably parallels the relative stability of the complexes between mercury (II), chloride ions and olefins, in this case 10-undecylenic acid, and *o*-aminothiophenol. The high affinity between mercury and sulfur, and sulfur-bonding ligands confers very high stabilities to their complexes with mercury (II) (*15*). Following these considerations, the *o*-aminothiophenol–mercury complex should have a higher stability constant with respect to the 10-undecylenic acid–mercury complex. This hypothesis is confirmed by the different chemical behavior of the two systems in the reactions with hydrogen chloride solutions: release of mercury chloride species from 10-undecylenic acid, no release from *o*-aminothiophenol. Because of the expected high stability constant of the *o*-aminothiophenol–mercury complex, the system cellulose–*o*-aminothiophenol was tested in a nearly saturated condition to be sure to have Hg^{2+} free ions in solutions also in the first samples. In this way, the high scavenger power of the *o*-aminothiophenol derivative and the high stability constant of the complex with the mercury are enhanced.

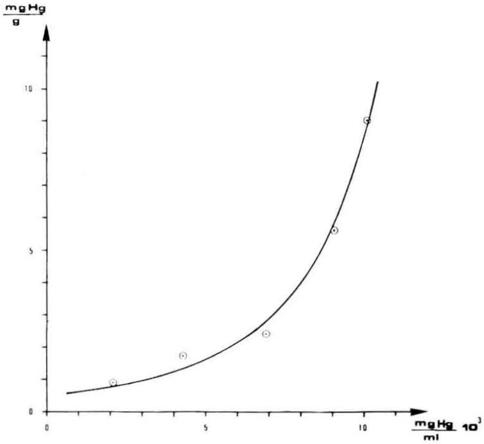


Figure 2. Adsorption isotherm of celyte cellulose 10-undecylenate support (t = 30 ± 0.1 °C). Mg Hg adsorbed per gram of support vs. soluble Hg (mg Hg/ml 10^{-3}) at equilibrium

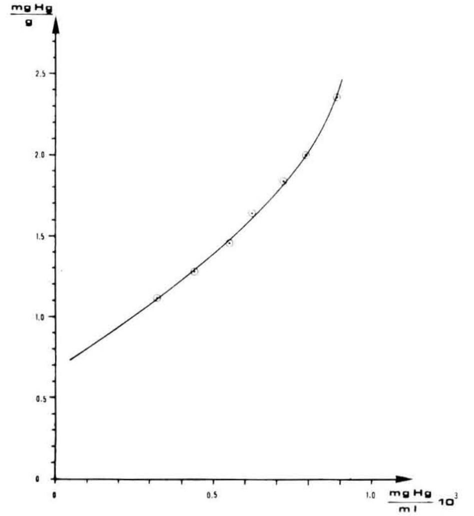


Figure 3. Adsorption isotherm of cellulose *o*-aminothiophenol derivative (t = 20 ± 0.1 °C). Mg Hg adsorbed per gram of support vs. soluble Hg (mg Hg/ml 10^{-3}) at equilibrium

A valid operational scheme for purification could be (*i*) removal of most of the Hg^{2+} ions by elution through a column containing cellulose 10-undecylenate celyte support; because of the reversibility of the system, most of the sorbed mercury can be recovered, (*ii*) elution of the effluent from (*i*) through a column containing the cellulose *o*-aminothiophenol derivative to obtain irreversible capture of the residual Hg^{2+} ions in solution. These procedures might offer a useful tool for the removal of Hg^{2+} ions from very dilute aqueous solutions (0.5 mg Hg/ml 10^{-3}) and can lower their concentration to 0.05 mg Hg/ml 10^{-3}. Further studies on these systems are in progress in our laboratories to test the efficiency of these supports toward the capture of cadmium, iron, lead, and other heavy metals from aqueous solutions.

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CORRESPONDENCE

SIR: The article, "Evaluating Environmental Impacts of Stack Gas Desulfurization Processes" [*ES&T*, **10,** 54 (1976)], attempts to assess the impact of considering secondary sources of pollution on the relative merits of five stack gas desulfurization processes. Unfortunately, the author's choice of basic data (particularly Table II) leads to seriously erroneous conclusions regarding these secondary sources. The analysis, based on Table I, is intended to apply to a new coal-fired generating station of 500 MW capacity so the use of pollutant generating factors from existing stations in 1972 is completely inappropriate; their use does not recognize that the major part of the utilities requirement would be provided by the plant itself, which would be subject to new source performance standards.

In addition, many of the costs associated with control to these levels of emission are already included in the given operating costs since control is frequently achieved through internal recycle of process waste streams. The costs then appear as incremental increases in equipment size and operating costs; thus, total costs associated with these secondary sources should include the costs of control, to the extent they are not already included in operating costs, for a major fraction of the pollutant plus an environmental cost for the actual emission. Viewed in this manner, the conclusions concerning the impact of secondary sources would be considerably different from those arrived at by the author. Relative to the large uncertainties associated with the total costs of these processes, particularly capital costs, byproduct cost/value and those related to reliability, assessments (revised) for secondary sources will be much less significant than is estimated by the author.

Incidentally, although "M" generally means 10^3 in the article, it appears to mean 10^6 in at least two places (Fuel, in Table II, and annual cost, in Table V). Also, in Table II, the particulate emissions are not realistic for existing utility sources, as shown by Table 4 of the author's reference *8*, or for gaseous and liquid fuels.

Thomas F. Evans

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SIR: The use of the 1972 pollutant-generating factors for utilities (Table II) in calculating the secondary effect is considered inappropriate by Dr. Evans on the ground that the major utilities requirements of a plant designed to meet the new source performance standards would be provided by the plant itself. When all utilities requirements are supplied within the plant, the plant would be engaged in the production of both *final* utilities (which are delivered to the users) and *intermediate* utilities (which are used as inputs within the plant). The *final* output wastes, defined as the pollutants/wastes that cannot be reduced through recycling within the plant, would then include the pollutants/wastes from both the primary and secondary sources. Hence, there is no need to estimate the pollutants/wastes from the secondary sources separately. In this case, control processes can be evaluated by comparing their *final* output wastes from the production of a *same* given amount of *final* utilities.

However, if the secondary pollutants/wastes are to be estimated separately from the primary pollutants/wastes, in spite of the fact that the *intermediate* utilities are produced within the plant, the use of new pollutant factors would leave out the very indirect effect this paper attempts to capture. The extra utilities required for a control process cannot be produced with less pollutants without adding an extra burden to the control process. Additional inputs (and hence more pollutants) are required for the control process to produce these *intermediate* utilities in the less polluted way.

It is recognized that the use of the 1972 data is not totally satisfactory. They tend to result in the overestimation of the secondary effect of utilities when the new performance standards achieved through the control processes would reduce the overall pollution level—i.e., the total environmental pollution is less with control than without control.

As to the units for fuel in Table II and annual cost in Table V, they are indicated by the notation $\bar{M}$ (with bar), which means 10^6.

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SIR: We wish to take exception with the line of reasoning and conclusions presented by Chameides and Stedman in their article, "Ozone Formation from NO_x in 'Clean Air' " [*ES&T*, **10,** 150 (Feb. 1976)]. Chameides and Stedman presented a photochemical model to explain occurrence of elevated levels of O_3 (>80 ppb) in rural areas in terms of photochemical reactions of natural methane and urban NO_x. The authors' findings suggest, implicitly, at least, that the only controllable factor causing oxidant formation in rural areas is anthropogenic NO_x. Such an implication is extremely important from a control standpoint and prompted us to submit the following critique on the Chameides-Stedman work and conclusions.

Key components in the Chameides-Stedman work and reasoning are:

- Using a 52-reaction step photochemical model for the atmospheric methane/NO_x reaction systems, the authors estimated the concentrations of O_3 expected to form in rural air contaminated with urban NO_x, and found the predicted O_3 concentrations to be comparable to those observed.

- Existing smog chamber evidence—contradicting the authors' model predictions—was dismissed by the authors as being unreliable.

We feel that the authors' model predictions are highly questionable and that dismissal of the smog chamber evidence is not justified, for the following reasons:

The photochemical model used by the authors cannot predict absolute concentrations of the oxidant product in the real atmosphere with confidence, for several reasons. First, predictions are subject to uncertainty because of uncertainties associated with the reaction mechanism, with the numerical values of the rate constants involved, and, most importantly, with the simplifying assumptions used by the authors to solve the model's kinetic equations. To illustrate this point, we attempted to duplicate the authors' results using currently accepted mathematical modeling techniques. Ozone yields were calculated for a methane/NO_x/CO system with initial concentrations similar to those in the authors' systems depicted in Figure 4. The reactions and rate constants used were similar but not identical to those used by the authors. The calculation yielded a maximum O_3 concentration of 16 ppb, compared to the 80 ppb or more predicted by the authors for similar levels of CH_4 and NO_x.

In an effort to isolate the main cause of disagreement, we recomputed the ozone yields for the systems depicted in Figure 4A and B, this time duplicating—as best as we could judge from the authors' article and given references—the authors' model, rate constants, and initial conditions, but using the Gear method (*1*) rather than the authors' "steady state approximation" method, for solving the model's kinetic equations. Our simulations gave ozone yields of 12 and 16 ppb, respectively, for the initial conditions depicted in Figure 4A and B of the authors' article. Thus, it appears that the authors' use of steady state assumptions—shown recently to be of questionable validity (*2*) for even the very short-lived species—may have been the cause of the authors' erroneously high ozone predictions.

Model predictions of absolute ozone concentrations are also subject to errors because the models presently available do not provide for reactant and product losses in processes other than the atmospheric chemical reactions. Thus, losses of NO_2 and O_3 on surfaces are known to be significant and widely varying, but have not been quantified yet. Such losses, if ignored, can only cause the model-predicted O_3 concentrations to be erroneously high.

The specific model predictions made by Chameides and Stedman do not justify the authors' conclusions for yet another reason. The authors' calculations were for rural air mixed with NO_x-rich urban air, ignoring the organic pollutants that unavoidably accompany urban NO_x. While it is true that reacted urban air is depleted of the most reactive organics, the less reactive—but certainly more reactive than methane—urban organics as well as organic reaction products are certain to accompany the residual urban NO_x into the rural areas. In fact, reacting ordinary urban air will be depleted of NO_x before it is depleted of its organic compounds—a fact that is attested to by aerometric data (*3*), smog chamber data (*4*), and photochemical model data, all showing that the hydrocarbon-to-NO_x ratio increases with reaction time. This is not to suggest that the urban organics that unavoidably accompany the urban NO_x eliminate or even lessen the oxidant production from the methane chain. Rather, it is to submit that if and when urban NO_x finds its way into a rural area, then urban organics will also be there to react and form ozone.

Considering the uncertainty of the photochemical model predictions of absolute ozone concentrations in the real atmosphere, and the unavoidable presence of urban nonmethane organics in urban-rural air mixtures, it follows that the methane contribution to rural ozone formation can be determined reliably only relative to the contribution of the companion nonmethane organics. Such determinations were made here using the EPA photochemical model. Specifically, the EPA model was used to predict ozone levels from irradiated hydrocarbon/NO_x systems including and excluding 1.4 ppm of methane. Results showed the methane-containing mixture to yield more ozone but only by about 1%. Such results clearly refute the authors' suggested conclusions that the rural O_3 can be caused wholly and solely by the methane/NO_x system.

Smog chamber data also show the methane to be incapable of the high oxidant yields predicted by the authors' model (*5*). The authors, however, dismissed such data, contending that chamber testing of the less reactive organics gives erroneously low O_3 concentrations "since radical losses to the walls become a significant interference". Such a contention represents only a hypothesis and clearly contradicts existing evidence and the viewpoint from most smog chamber researchers. Smog chambers of ordinary design, that is, made of aluminum or Pyrex or Teflon film, and of several cubic feet capacity, are known to produce suspiciously high levels of O_3 out of a few pphm of HC–NO_x reactants (*6*). Such a suspected smog chamber effect has been referred to as "dirty chamber effect" (*7*) and more recently was attributed by Niki and Weinstock to a "smog chamber source of OH radicals" (*8, 9*). All in all, although the smog chamber wall effect is not clearly understood, the evidence available suggests that for ordinary smog chambers, such effects, if any, would tend to cause higher rather than lower O_3 yields in lower reactivity systems.

In conclusion, explaining rural O_3 in terms of methane–urban NO_x reactions alone is unsupported by the evidence available. Although not all causes of elevated (i.e., >0.08 ppm) rural O_3 have been established with confidence, the composite of evidence based on trajectory analysis (*3*), ozone–acetylene correlation (*10*), and smog chamber and modeling data all but make it certain that one such cause is reactions involving transported inorganic *and organic* urban pollutants. Natural hydrocarbons (e.g., terpenes) may be another conceivable cause; however, methane cannot be included among them.

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SIR: In a recent paper, Chameides and Stedman (*1*) postulated that oxides of nitrogen (NO_x) transported from urban centers interact with the natural methane (CH_4) oxidation cycle to yield ozone (O_3) concentrations above the National Ambient Air Quality Standard (NAAQS) of 0.08 ppm. A photochemical model was used to demonstrate the proposed effects. If their results and conclusions were valid, they would have a major impact on air pollution control strategies. The conclusions that "the highly reactive heavier (than methane) hydrocarbons do not play a role in the production of ozone in rural areas" would be of extreme importance because the current oxidant control strategy of EPA is to control nonmethane hydrocarbons (NMHC). NO_x is controlled only to the extent necessary to meet the NAAQS for nitrogen dioxide (NO_2).

The results of Chameides and Stedman are contrary to experimental evidence for CH_4 and NO_x behavior (*2*) and to other modeling results (*3*). They presented no evidence to support their statement that smog chamber experimental results for less reactive hydrocarbons are unreliable because of radical loss to the walls. In fact, Chameides and Walker (*4*) concluded that heterogeneous processes were not likely to be significant in the case of hydroperoxy radicals. It is more likely that smog chamber surfaces provide an effective site for the occurrence of heterogeneous reactions (e.g., metal surfaces and nitrogen oxides reaction) and act as a source of low level contaminants such as higher molecular weight hydrocarbons, aldehydes, and nitrogen compounds. These "wall effects" tend to *increase* the oxidant yields in low reactivity smog chamber experiments.

A key factor to be considered when assessing the validity of Chameides and Stedman's results is that they did not solve the kinetics model directly, but solved a model of the model. That is, they introduced a different representation of the chemical events by assuming that the two most important species, hydroxyl (OH) and hydroperoxy radicals (HO_2), as well as others, were in photochemical equilibrium. This technique of dealing with stiff systems of differential equations is usually called the quasi-steady-state-assumption (QSSA), and it has been shown to be an unreliable approach for solving atmospheric HC and NO_x kinetics systems (*5*).

To determine if the QSSA made by Chameides and Stedman could have affected their predictions, we repeated the entire simulation, but used the widely accepted Gear algorithm for systems of stiff differential equations (*6*) to provide a direct numerical solution of the mechanism. The urban NO, NO_2, and O_3 levels at 03, 06, 09, and 12 h, as determined from their graphs, were used as the initial conditions for the mechanism presented by Chameides and Walker (*4*). As in the Chameides and Stedman simulation, the rate constants were taken from Hampson and Garvin (*7*), and the concentrations of the following species were assumed to be constant: methane, 1.5 ppm; hydrogen, 0.5 ppm; and water vapor, 18 000 ppm. In addition, no urban hydrocarbons or carbon monoxide was "transported" out of the urban environment, in conformance with the assumptions of Chameides and Stedman. The results of these four simulations are presented as linear plots in Figure 1. They differ markedly from those of Chameides and Sted-

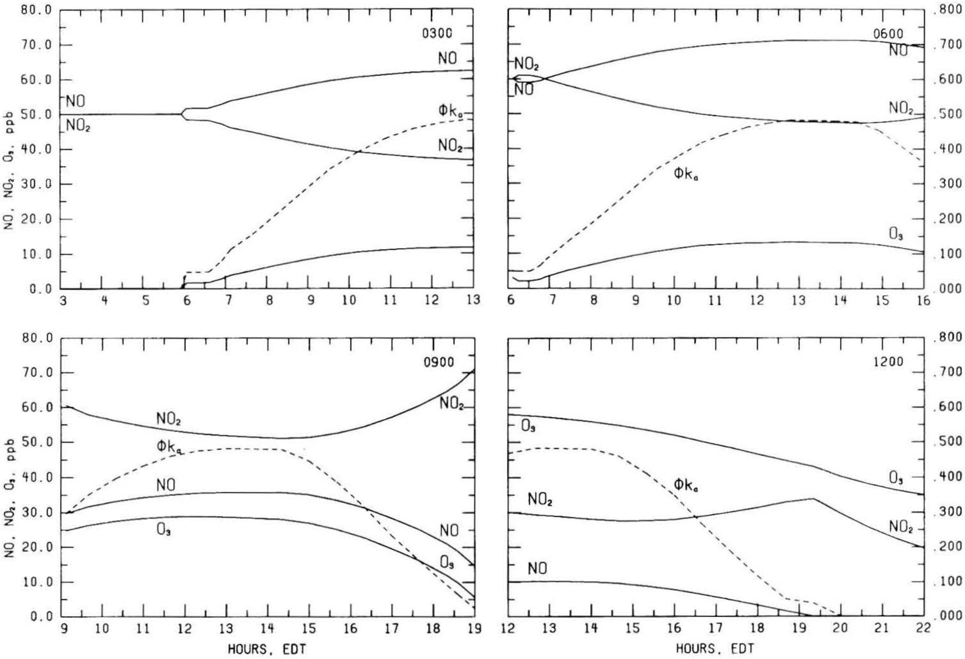

Figure 1. Calculated time variation of O_3, NO, and NO_2 in air mass after passing over urban pollution source starting at 03, 06, 09, and 1200 h

man (Figure 3, ref. *1*), often by a factor of 10 in O_3 concentrations. This was not unexpected, since under the QSSA the radical concentrations can be several orders of magnitude in error (*5*). The very fast initial rise of O_3 and the relatively fast loss of NO_x in their model are symptomatic of this type error.

The impact of these four urban systems on a rural site 10 h downwind, assuming no further emissions or dilution, is shown in Figure 2. Chameides and Stedman (Figure 5, ref. *1*) show a very rapid rise of O_3 beginning at 1300, whereas our results indicate a *decrease* below their 40-ppb background level and a small rise between 19 and 22 h. Figure 1 indicates that this rise occurred, not because of O_3 synthesis due to CH_4, but because of the partial survival of the urban initial condition of ~60 ppb O_3.

It would thus appear that the results reported by Chameides and Stedman are artifacts of the QSSA; therefore, their conclusion that NMHC's are not necessary for the formation of O_3 above the NAAQS is unsupported.

In addition to difficulties in the solution of the model, there are other aspects of their approach that require comment. The situation assumed by Chameides and Stedman was essentially that of a nonsteady-state plug-flow reactor 155 miles long with a 10-h residence time (a flow rate of 15 mph). This cannot be considered as characteristic of most rural high oxidant situations since trajectory analyses of air parcels arriving at a rural sampling site for high oxidant days vs. low oxidant days do not show any definite patterns. The rural high oxidant situation is further characterized by multiday persistence over a very large area, usually near the center of a high-pressure area with characteristically light winds. The NMHC's range typically from 0.5 to 1.0 ppmC, and NO_x from 6 to 10 ppb (*8*, *9*). These characteristics suggest in situ oxidant formation rather than transport of oxidant from a nearby (i.e., 10-h time) urban center. Outdoor smog chamber work at the Research Triangle Institute and at the University of North Carolina demonstrates that a 95% diluted and "spent" urban smog system can readily generate O_3 above 0.08 ppm after 2 and 3 days of natural irradiation (*10*, *11*). Sickles has shown that isopentane and NO_x systems subjected to sunlight irradiations can exceed the O_3 NAAQS with initial concentrations as low as 0.2 ppmC NMHC and 20 ppb NO_2 (*12*). This system is also capable of "storing" more than 50% of the O_3 generated in a given day's exposure. Most evidence indicates that the rural high oxidant situation may be NO_x controlled, but hydrocarbons other than CH_4 are required to achieve O_3 greater than 0.08 ppm. The situation is clearly not as simple as that suggested by Chameides and Stedman.

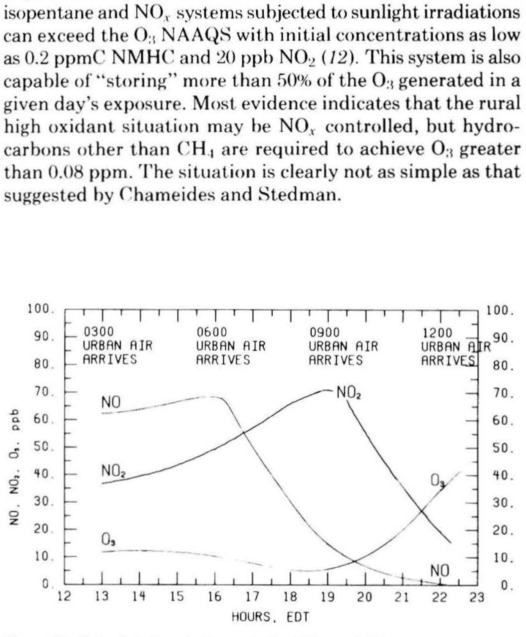

Figure 2. Calculated variations of O_3, NO, and NO_2 at rural site 10 h downwind of urban pollution source

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SIR: Dimitriades et al. and Jeffries and Saeger have argued against our mechanism (*1*) for the production of high levels of ozone in rural areas. Their objection is largely based on clear discrepancies between our model results and theirs. They suggest that the fault lies in our use of the quasi-steady-state-assumption, which, they claim, tends to yield unrealistically high radical concentrations. They also argue that our results are contrary to smog chamber data.

However, we believe our predictions can be justified by comparison with measurements and the predictions of others. Truly unpolluted air may not be found in Dearborn, Mich.; however, our model predicts OH radical concentrations in agreement not only with Wang et al. (*2*) but also, when the proper input data are used, with the unpolluted upper tropospheric measurements of Davis (*3*). If, as Wang et al. have observed, OH is present in the summer daytime atmosphere at concentrations of the order of 10^7 cm^{-3}, significant quantities of O_3 could be generated from our assumed concentrations of CH_4, CO, and H_2 of 1.5, 0.65, and 0.5 ppm, respectively. While CO is a product of the oxidation of CH_4, we recognize that a CO concentration of 0.65 ppm, appropriate for the continental U.S. (*4*), represents an anthropogenic input. At these concentrations HO_2 and CH_3O_2 radicals are produced at a combined rate of about 5–10 ppb h^{-1}, as shown in Table I. For NO concentrations of the order of 50 ppb, this production will result in an equivalent O_3 production rate of about 5–10 ppb h^{-1} as predicted in our model calculations (*1*).

While smog chamber data would appear to contradict our calculations, Demerjian et al. (*5*) point out that significant problems arise in any attempt to interpret smog chamber data. This may arise partly from unreproducibility, since no published data are yet available which show either that any one chamber can quantitatively repeat the same data a year or two later, or, more importantly, that any two smog chambers can obtain the same results from the same standard experiment. Bufalini et al. (*6*) in their study of contaminated smog chambers state that "as long as the walls of the chambers are not cleaned between runs, oxides of nitrogen will be liberated" and "we believe, however, that methane and carbon monoxide play a significant role in the formation of ozone from irradiated air in a dirty chamber". The dirt in this case was low levels of NO_x, and the methane and CO were "present even in zero grade air".

Demerjian et al. (*5*) model air containing 10 ppm CO and observe an effect equivalent to an ozone formation rate of about 40 ppb/h of ozone. Our system is roughly equivalent to 1 ppm CO which scales to an ozone formation rate of 4 ppb/h, in reasonable agreement with our calculations considering the necessarily approximate comparison.

We do not consider that CO and methane are the sole carbonaceous contributors to rural oxidant or even to the "dirty chamber effect"—merely that they are highly significant. This point is made very clearly using the relative rates of OH attack as described by Calvert (*7*) to some rural hydrocarbon data from Kane Pa (*8*). Such a calculation indicates that about 25% of the total OH attack is due to CO and methane. Formaldehyde, another member of the methane oxidation chain, although included in our model calculations, was not included in this analysis and may also be important. Note that the fact that rural oxidant levels are at times found to be in excess of 200 ppb is reasonably consistent with this analysis, since our simplified calculations neglecting nonmethane hydrocarbons yield ozone levels of at most 100 ppb.

Dimitriades et al. are correct in pointing out the difficulties in using model results to reliably predict levels of oxidant produced (although similar criticisms can be raised against smog chamber data). For instance, uncertainties in several key reaction rates imply a rather large uncertainty in the ozone enhancement we calculate, as illustrated in Figure 1. When we treat ozone photolysis to produce $O(^1D)$, $O_3 + h\nu \rightarrow O(^1D) + O_2$, as a constant at $5 \times 10^{-6}\ s^{-1}$ [the value listed as a diurnal, seasonal average by Chameides (*9*)], we obtain, using our QSSA method, the solid curve in Figure 1. This result is essentially identical to the Gear routine plots of Jeffries and Saeger and the results of Dimitriades et al. When the ozone photolysis rate is treated diurnally [with a peak value of $2 \times 10^{-5}\ s^{-1}$, similar to that used by Demerjian et al. (*5*)], we obtain the dashed curve of Figure 1. The enhancements are somewhat smaller than originally calculated (*1*) (Curve 3B) because we now solve the $NO/NO_2/O_3$ system in a more exact manner by integrating equations for $d[n(NO) + n(NO_2)]/dt$, $d[n(O_3) - n(NO)]/dt$ and applying the photostationary state equation. We are also using $3 \times 10^{-12}\ cm^3\ s^{-1}$ for $NO_2 + OH \xrightarrow{M} HNO_3$ (*10*) and include $HO_2 + NO_2 \rightarrow HONO + O_2$ with a rate constant of $3 \times 10^{-14}\ cm^3\ s^{-1}$ as recommended by Hampson and Garvin (*11*); this brings the total reactions considered to 43 (not 52 as we had incorrectly stated). Finally, when we use $1.2 \times 10^{-13}\ cm^3\ s^{-1}$ for $HO_2 + NO_2 \rightarrow HONO + O_2$, as measured by Cox (*12*), we obtain the dash-dotted curve with an ozone buildup of only about 40 ppb.

Clearly, more laboratory and field work is necessary before the problem of rural ozone events can be understood; however, at this time we do not agree that methane and its oxidation products "cannot" play a role in rural ozone events.

Table I. HO_2 and CH_3O_2 Radical Production Rates from CH_4 Oxidation Chain[a]

	Species			
	CH_4	CO	H_2	Total
Concentration, ppb	1500	650	500	
$k(OH)$ (*11*), $cm^3\ s^{-1}$	9×10^{-15}	1.4×10^{-13}	6.4×10^{-15}	
Effective HO_2 yield	~3	1	1	
$HO_2 + CH_3O_2$ formation rate, ppb/h				
$n(OH) = 1 \times 10^7\ cm^{-3}$	1.5	3.3	0.1	4.9
$n(OH) = 2 \times 10^7\ cm^{-3}$	3.0	6.6	0.2	9.8

[a] Formaldehyde, if produced only by CH_4 oxidation, is not a major factor; however, the presence and importance of formaldehyde from other sources cannot be ruled out.

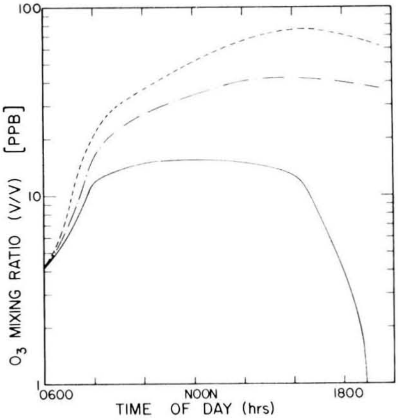

Figure 1. Calculated time variation of O_3 in air mass with initial conditions appropriate for 0600-h start (*1*)
Solid line obtained when $J(O_3 + h\nu \rightarrow O(^1D) + O_2) = 5 \times 10^{-6}\ s^{-1}$. Dashed-dotted line obtained when $k(HO_2 + NO_2 \rightarrow HONO + O_2) = 1.2 \times 10^{-13}\ cm^3\ s^{-1}$. Dashed line: standard model result (see text)

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INDUSTRY TRENDS

Union Carbide Corp. has announced that a $4 million wastewater treatment plant at its Marietta, Ohio, chemicals and plastics plant is on stream. The 1.7 mgd plant uses Union Carbide's UNOX treatment system.

Ecodyne, Ltd., Canadian subsidiary of **Ecodyne Corp.,** will provide more than $6 million worth of evaporator equipment for Zakłady Celułozowo-Papiernicze, a paper company of Kwidzyn, Poland.

Sasaki Associates, Inc. (Watertown, Mass.) has begun an intensive study of the environmental impact of constructing facilities for the 1980 Winter Olympics at Lake Placid, N.Y. Project cost is $250 000.

Lone Star Steel Co. (Dallas, Tex.) will provide its patented Steam-Hydro air cleaning equipment to Empire-Detroit Steel, Cyclops Corp., to handle 105 000 scfm. Expected efficiencies are 99.9% for particulates, and 99% for SO_2.

Envirex Inc. has been granted a patent on a new fiberglass rotary lift used with diffused aeration equipment for municipal and industrial wastewater treatment.

The Carborundum Co. is supplying a tertiary sewage treatment facility to the City of Sunnyvale, Calif., featuring the largest algae removal system in the U.S. Completion is scheduled for early next year.

DCE Vokes, U.S., has been formed at Louisville, Ky., as specialists in industrial air pollution control and in-plant dust control. It is a branch of a British company, DCE Vokes, Inc.

Commonwealth Associates (Jackson, Mich.) will do consulting and design work on an interconnected electric utility system for Empresa Nacional de Electricidad of Bolivia. Consultores Galindo Ltda. (Cochabamba, Bolivia) is working with Commonwealth on this project.

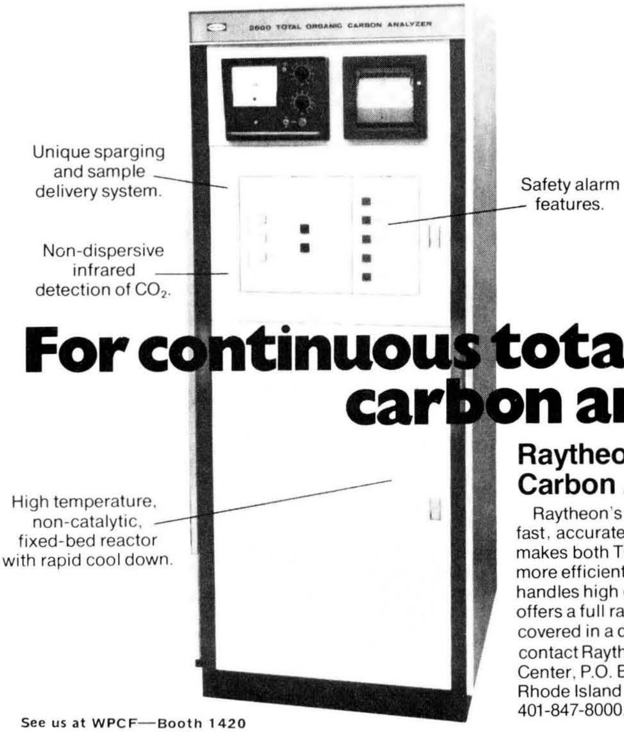
Parsons & Whittemore, Inc. (New York, N.Y.) is general contractor for the $73 million refuse-recovery energy plant with which Long Island Lighting Co. will generate 250 million kW/yr from resultant fuel, and the City of Hempstead (N.Y.) will have its waste (11 000 t/wk) processed for resource recovery.

Arthur W. Busch has established private practice of environmental engineering consulting in Dallas, Tex. Previously, Busch was chairman of the Department of Environmental Engineering at Rice University, and regional administrator of EPA Region VI.

Enviro-Test, Inc. has initiated operations at Westmont, Ill., to perform water analyses, general consulting, and general analytical services for the Chicago and midwest area.

Public Service Co. of New Hampshire has received a construction permit for a 2300-MW nuclear power plant at Seabrook, N.H., and has started site work. Full operation is expected by mid-1983.

PCP, Inc. (West Palm Beach, Fla.) is now a licensee under patents in plasma chromatography owned by Franklin GNO Corp. of West Palm Beach. Plasma chromatography can detect and measure ultra-



trace amounts of chemicals in the environment.

Wyle Laboratories (El Segundo, Calif.) received a contract of about $2.2 million from IBM to test and evaluate a solar house with heating and cooling at NASA in Huntsville, Ala. Four systems can be tested.

Dow Corning is "encouraged" by interest and action on its silicone-based PCB-substitute transformer fluid, particularly by market response, and by EPA's not having found any adverse health or ecological effects.

Drew Chemical Corp., a subsidiary of U.S. Filter Corp., offering products and services in water management and related fields, is expanding its Boonton, N.J., location by 16 000 ft^2 to increase technical service and support, and enhance product development.

Tracor, Inc. (Austin, Tex.) has received a $1 million contract from NOAA to develop and deliver 10 airborne systems for atmospheric research concerned with predicting the weather.

ERT (Concord, Mass.) has received a one-yr extension of its contract with the Manufacturing Chemists Association (Washington, D.C.) to investigate possible effects of fluorocarbons on the stratospheric ozone layer.

The **Electric Power Research Institute** (Palo Alto, Calif.) has signed a Memorandum of Understanding with ERDA to provide for broad R&D cooperation between the two organizations.

Alyeska Pipeline Service Co. announced that the forecast cost of $7.7 billion, to complete the system to an initial design capacity of 1.2 million bbl/d, is a 10% increase that includes weld/x-ray problems, lower productivity than projected, and other unanticipated needs.

Envirodyne, Inc. (Los Angeles, Calif.) has signed a $2.4 million, 2-yr contract dealing with the expansion and modernization of the Northside Sewage Treatment Works (400 mgd) for the Metropolitan Sanitary District of Greater Chicago.

Combustion Engineering's C-E Power Systems is offering a new spray tower absorber system for flue gas SO_2 removal that has less horsepower requirements because of a low draft loss. Removal efficiency is over 90%, according to C-E.

The **American Water Works Association** (Denver, Colo.) has approved Standard C708–76, which covers multijet water meters in $\frac{5}{8}$–2-in. sizes.

Enviroplan, Inc. (Rutherford, N.J.) will supply and run an air pollution and meteorological monitoring network, including quality control and training, for 4 coal-fired power plants of Cleveland (Ohio) Electric Illuminating Co.

Fuller Co. (Catasauqua, Pa.) will furnish a pneumatic conveying system to Reynolds Metals Co. (Richmond, Va.) for $500 000. The system will handle bulk alumina used to scrub gases at a Reynolds plant in Troutdale, Ore.

Monsanto Enviro-Chem Systems, Inc. was awarded a multi-million dollar contract by American Cyanamid Co. for design of a 1600-tpd sulfuric acid plant at Westwego, La. SO_2 emission standard compliance must be assured.

UOP-Kavag (W. Germany) will supply air pollution control equipment to be used in six large incinerators (up to 50 000 m^3/h) at a new mineral wool production complex near Lake Baikal, USSR.

Nalco Chemical Co. is offering a new organic chemical binder, known as Nalco 8820, to reduce windage losses of coal, slag, flue dust, and other such materials when they are in transit.

Clow Corp., maker of pipe, valves, and waste treatment equipment, has announced a $5 million plant modernization and expansion plan for its Foundry Division.

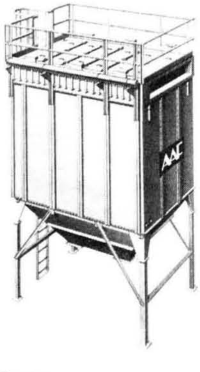
NEW PRODUCTS

pH meter electrode
Protective epoxy plastic body of the electrode extends beyond the membrane glass but still permits the membrane to make complete contact with the solution being tested. The unbreakable probe is used with the manufacturer's portable pH meter. L. G. Nester Co. **101**

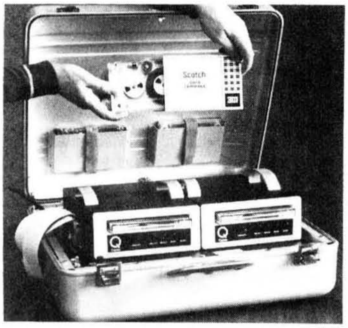
Organic waste digester
The material is a concentrate of non-pathogenic, broad-spectrum bacteria combined with enzyme culture systems that when activated serves as an organic waste digestive system. It can be used to reduce suspended solids in lagoons, ponds, holding tanks and other bodies of water. West Chemical Products, Inc. **102**

Respirable dust kit
Consists of a battery-powered pump with one or more sampling heads, a battery charger, spare battery, and several days' supplies of consumable items such as filter paper. The pump and head travel with the wearer for up to 10 h of mobile sampling. C. F. Casella & Company Ltd. **103**

Water quality monitoring system
The submersible system measures six parameters in coastal, inland, and ocean waters to depths of 300 m. It can be used on projects requiring continuous stationary operation from fixed shore stations or offshore platforms. Martek Instruments, Inc. **104**

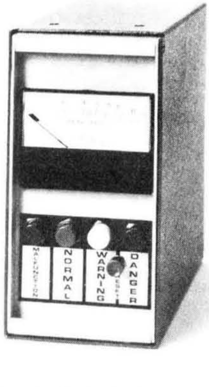


Dust collector
The down-flow fabric dust collector comes in 18 sizes from 770–6928 ft^2 of filter media with air flow capacities from 7000–70 000 cfm. The cleaning cycle is sequential and automatic. American Air Filter Company, Inc. **105**



Data storage unit
The portable digital cartridge recorder features a data storage system that uses a 3M data cartridge as the tape storage medium. The recorder comes with interfaces for minicomputers and microprocessors. The data rate is 6000 bytes/s and storage capacity is 2.88 megabytes. North Atlantic Industries, Inc. **106**

CO monitor/alarm
Continuously indicates the ambient level of carbon monoxide on a 0–300 ppm meter with an accuracy of ±10% of reading. The optional alarm horn is factory set to sound when the CO concentration exceeds 200 ppm, but it is adjustable from 10–200 ppm. Dynamation, Inc. **108**

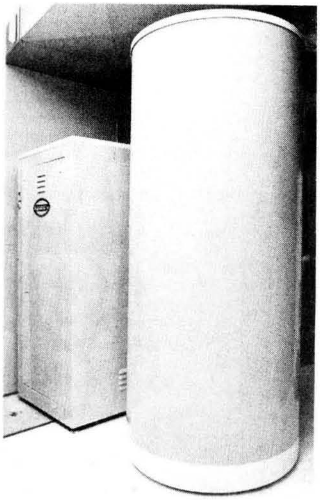


Hydrogen sulfide detector
The continuous monitoring, semi-conductor sensor has excellent specificity to H_2S, and two full adjustable alarm contacts. Control Instruments Corp. **109**

Hose and pipe couplings
Made from fiberglass-reinforced nylon, the couplings, which come in eight sizes from ⅜–1-in., are impervious to most chemicals and are stable at extreme temperatures. Andrews Industries. **111**

Airlock for baghouses
A rotary airlock with a 2-in. diameter shaft and flexible twin wiper blades that retain their flex characteristics at operating temperatures of up to 400 °F has been designed for baghouse dust handling systems. Standard Havens, Inc. **112**

Flowmeter
Measures flows to accuracies better than ±1% of actual volumetric flow from 1–25 ft/s. Suspended solids, entrained air and changes in fluid density or conductivity do not effect accuracy. Envirotech Corp. **113**



Water recycler
Designed for residential use, the manufacturer claims a 40–50% decrease in water consumption in the home. The system retrieves wastewater from tubs, washing machines and basins, chemically treats it for use for toilet flushing, lawn sprinkling, and other nonpotable purposes. It has been certified by the National Sanitary Foundation. Aquasaver, Inc. **114**

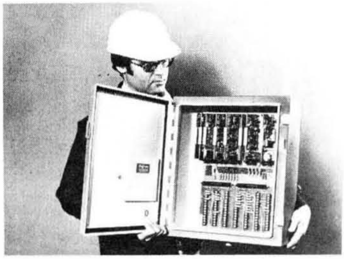
Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

Membrane filter funnels
The 25 mm polysulfone plastic funnels, in 50 and 200 ml capacities, are designed for small volume vacuum filtrations of liquids and for use in particulate matter analyses. Twist-lock coupling links the funnel to the stem. Gelman Instrument Co. **110**

Coliform incubator/bath
Set point temperature is maintainable at 44.5 ± 0.2 °C. Two racks provide capacity for 288 membrane filter cultures. GCA/Precision Scientific **115**

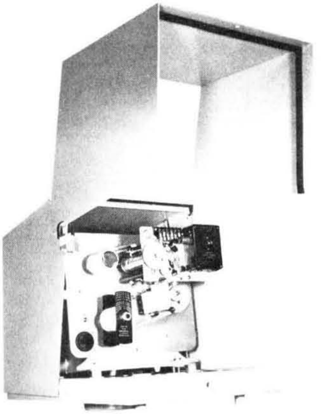
Pumps
Self-priming rotary pumps have flow rates of 0.25–3.0 g/min and can handle thin or viscous liquids. Elders Industries Inc. **121**

Water sampling system
The system includes a monitor that measures continuous liquid flow, a totalizer and strip-chart recorder, a non-contact ultrasonic sensor to detect flow, a water sampler, and a sampler controller that regulates collections on a lapsed-time or proportional-to-flow basis. Environmental Measurement Systems **107**



Remote data station
This remote data acquisition and control station finds application in water and wastewater monitoring and control facilities. Leeds & Northrup Co. **116**

Elevating system
The enclosed system was designed to safely handle radioactive materials; it specially conveys radioactive powders from a drier to a calciner. The elevator handles these powders at temperatures from 250–300 °F. The Bucket Elevator Co. **117**



Tide gauge
Records tide level changes within a 50-ft range on a 16-bit punched paper tube. Punching is timed by a timer selectable in 5-min increments up to 1 h. Leupold & Stevens, Inc. **119**

Pipe coating
The polypropylene copolymer coating offers increased temperature and corrosion resistance. Coated pipes and fittings may be used in applications such as blast furnace fly ash slurries, power plant stack gas scrubbers, and acid regeneration waste lines. Kearney Fluid Equipment, Inc. **120**

Dual stream SO_2 monitor
The instrument can continuously monitor sulfur dioxide from two separate sources simultaneously. Range is from 0–1 ppm full scale to 0–2000 ppm full scale. Theta Sensors, Inc. **118**

Rinse water controller
This automatic rinse water make-up controller adds fresh water only when the electrical conductivity of the rinse solution exceeds a pre-selected set point. Pollutronics, Inc. **122**

Nitrogen analyzer
Modular unit can also be expanded to analyze for trace sulfur and halogens. The instrument will accept liquid, solid, and gas samples. It will analyze for trace amounts of nitrogen in the 0–1000 ppm range. Envirotech Corp. **133**

Gas/vapor detector
The system with a variable number of separate channels is contained in a central control station. Each channel, a separate instrument, is connected to separate detectors mounted in predetermined hazardous locations. Teledyne Analytical Instruments **124**

Sulfur dioxide absorbents
Solid polymeric adsorbents to remove different concentrations of SO_2 from ambient air can be fabricated in granular, pellet, or coated-filter substrate form. These materials are still in the developmental stage and inquiries regarding their potential application should be directed to the company. Union Carbide Corp. **126**

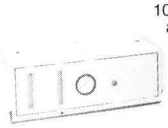
Dissolved oxygen analyzer
The manufacturer claims that the unit provides accurate reading of dissolved oxygen over ranges as low as 0–20 ppb. The probe's response is linear, making calibration easier. If finds application in boiler feedwater measurements. Rexnord **127**

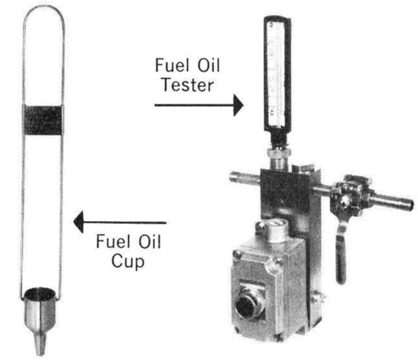
Flowmeter
The borosilicate glass metering tube is mounted in an acrylic protective support block with aluminum side frames. The 150-mm scale is fused directly on the tube. The floats are black glass, stainless steel, or sapphire. Matheson Instruments. **134**

Respirators
Continuous-flow respirators are designed to supply clean respirable air up to 300 ft from the air source. These units are NIOSH approved and are designed to protect workers against harmful atmospheres that are not immediately dangerous to life. ESB, Inc. **130**

Transformer liquid
This silicon transformer liquid is offered as an alternative to PCB-containing askarels. The manufacturer claims that the liquid is environmentally safe, and is resistant to fire and explosion, but has excellent electrical performance. Dow Corning **131**

pH/ORP/conductivity analyzer
The instrument may be obtained in different configurations—with meter, recorder or digital readout; analog outputs; on/off control; and proportional plus reset controllers. Great Lakes Instruments, Inc. **125**





American Chemical Society

Advances
Symposia
Reprint
Collection

TITLES IN ENVIRONMENTAL CHEMISTRY

American Chemical Society, 1155 16th St., N.W./Wash., D.C. 20036

Removal of Trace Contaminants from the Air
Victor R. Deitz, Ed.

Sixteen chapters provide critical and in-depth coverage of air pollution characterization and removal. The collection stresses interactions among particulates and gas phase contaminants; pesticides; occupational contaminants; cigarette smoke and aerosol filtration; sulfur dioxide; trace gas adsorption; nitrogen oxides; and high ozone concentrations.

207 pages. Cloth. (1975) $17.25

Approaches to Automotive Emissions Control
Richard W. Hurn, Ed.

Nine chapters spotlight current developments toward the goals of lower emissions and greater fuel economy: the impact of automotive trends and emissions regulations on gasoline demand; gaseous motor fuels; fuel volatility, the pre-engine converter; and low emissions combustion engines.

211 pages. Cloth. (1974) $12.95

Air Pollution
Collected by D. H. Michael Bowen

Contains 38 articles from Volumes 3-6 of *Environmental Science & Technology.* Laws and regulations, specific pollutants and standards, monitoring, control methods, and transportation.

138 pages. Hard. (1973) $7.50
138 pages. Paper. (1973) $4.50

Solid Wastes—II
Collected by Stanton S. Miller

Thirty-three articles from Volumes 4-7 of *Environmental Science & Technology* report on federal, state, and local government projects; recycling and resource recovery; auto hulk disposal; plastics; scrap iron and tires; industrial sewage and sludge; and solid waste treatment technology.

"The book should be helpful to anyone who needs to be brought up to date in a hurry."
Reuse/Recycle (1975) **9**, 11

118 pages. Hardback. (1973) $7.50
118 pages. Paperback. (1973) $4.50

Pollution Control and Energy Needs
Robert M. Jimeson and Roderick S. Spindt, Eds.

Nineteen papers focus on energy demands vs. primary fuel supplies and the effectiveness of technologies that have been developed to meet environmental regulations. Topics include natural energy reserves, control of SO_x and NO_x, H-Oil desulfurization, sulfur oxides removal from stack gases, RC/Bahco system, effect of desulfurization methods on ambient air quality, and several available processes.

249 pages. Cloth. (1973) $16.95
249 pages. Paper. (1973) $9.95

Solvents Theory and Practice
Roy W. Tess, Ed.

Thirteen papers present the latest application formulas and techniques to combat pollution from solvents. Predicted compositions of resin solutions, solvent selection by computer, prediction of flash points for solvent mixtures, epoxy resin coatings, photochemical smog reactivity of solvents, solvents in electrodeposition coatings, polyamide resin solubility parameters, and solubility characteristics of vinyl chloride homopolymers, copolymers, and terpolymers.

227 pages. Cloth. (1973) $15.75

Catalysts for the Control of Automotive Pollutants
James E. McEvoy, Ed.

Current research by auto makers, catalyst companies, universities, and chemical and petroleum companies on all aspects of catalytic conversion to reduce automotive emissions. Emphasis is on analytical methods, mechanisms of catalytic removal, and catalysts themselves. Specific topics examined in fourteen papers include variation of selectivity, catalyst poisoning, the nature of the catalyst support, and others.

199 pages. Cloth. (1975) $19.95

Trace Elements in Fuel
Suresh P. Babu, Ed.

The latest research results on these often-toxic emissions cover their origin, the quantities in which they escape into the atmosphere, determination methods, and physiological effects. Specifically, fifteen chapters detail mineral matter and trace elements in coal; coal pretreatment and combustion; mercury and trace element mass balance; and environmental toxicology.

216 pages. Cloth. (1975) $16.50

Trace Elements in the Environment
Evaldo L. Kothny, Ed.

Nine chapters examine the geochemical cycle of trace elements in the environment. Boron, zinc, and selenium are discussed, as well as atmospheric pollutants, marine aerosol salt and dust, particulates, inorganic aerosols, S, V, Zn, Cd, Pb, Se, Sb, Hg. Includes methods of identification, separation, and measurement.

149 pages. Cloth. (1973) $12.50
649 pages. Paper. (1973) $7.25

Environmental Chemistry, Vol. 1
Senior Reporter: G. Eglinton

A review of the literature up to mid-1973 covering stable isotope studies and biological element cycling; environmental organic chemistry of rivers, lakes, bogs, marshes, swamps, oceans, fjords, anoxic basins; hydrocarbon distribution in the marine environment; DDT and PCB; organic chemistry of 2, 4-dichlorophenoxyacetic acid.

199 pages. Cloth. (1975) $22.00

Sulfur Removal and Recovery from Industrial Processes
John B. Pfeiffer, Ed.

Sixteen chapters form a consolidated reference source of sulfur removal and recovery methods concentrating on recovery techniques from sources other than power plant stacks. Emissions from smelter gas streams and Claus units are discussed, and seven scrubbing processes are described. Companion volume is No. 140.

221 pages. Cloth. (1975) $16.95

Marine Chemistry in the Coastal Environment
Thomas M. Church, Ed.

Forty-one chapters cover topics in six major areas: physical, organic, and tracer marine chemistry; estuarine geochemistry; hydrocarbons and metals in the estuarine environment; ocean disposal forum; applications and resources in marine chemistry; and organic and biological marine chemistry.

710 pages. Cloth. (1975) $35.75

Water Pollution
Collected by Stanton S. Miller

One-hundred-six articles from Volumes 4-7 of *Environmental Science & Technology* discuss federal and state policy; how, and to what extent military, business, and industrial communities are acting to implement new laws and standards; monitoring, specific pollutants, tertiary treatment, drinking water, microstaining, desalination, electrolysis, adsorption, and sewage treatment.

317 pages. Hardback. (1974) $15.00
317 pages. Paperback. (1974) $9.50

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NEW LITERATURE

Scrubber improvement. Bulletin 746 outlines engineering programs that reduce scrubber sludge volume by 50%, cuts suspended solids, minimizes nozzle clogging, and improves performance. Case histories are given. Betz **151**

Non-clog pumps. Bulletin 30B1 lists Series 3000 recessed impeller pumps whose design overcomes clogging and corrosion in heavy-duty pumping applications. Capacities to 2500 gpm. Fybroc, Inc. **152**

Chromatography. Catalog 18 lists many materials for gas, liquid, and thin-layer chromatography. There is a new section on pollution analysis supplies. Analabs, Inc. **153**

Topographic maps. Literature describes and lists over 300 maps of the U.S. mainland and Hawaii. These are useful for land-use planning, oil exploration, forestry, and other applications. Hubbard Scientific Co. **154**

Gas chromatography. New Gas Chromatography Bibliography covers techniques, methodology articles, sampling systems, columns, detectors, and data systems. Applications listed include environmental analysis. Perkin-Elmer **155**

Oxygen/BOD. Catalog, with specifications and prices, lists full line of battery-operated portable instruments for measuring dissolved oxygen and BOD. To 20 ppm with ±0.1 ppm accuracy. Temperature measurements −5 to +45 °C. Yellow Springs Instrument Co., Inc. **156**

Solar Collectors. Bulletin SE 1-76 details available data and questions still to be answered concerning solar collectors. It lists limitations that should be known to designers and builders to solar systems. Filon, Division Vistron Corp. **157**

Sewer line cleaning. Brochure explains how new vacuum-cleaning system can remove solids and liquids from sewer lines at the same time with 50% more productivity and at 50% less cost. Aquatech-Moro, Inc. **158**

Isomer separation. Applications circular describes separation and identification of isomer mixtures by gas chromatography/infrared techniques. Sadtler Research Laboratories, Inc. **159**

Level control. Booklet, "So you think you have no level control problems," tells engineers why they should consider use of the new Universal Level transmitter. Drexelbrook Engineering Co. **160**

Water testing "hotline." Bulletin NES-12 describes company's analytical services for water and wastewater, and announces a telephone "hotline" service—24 h/d—for accommodating urgent customer needs or requests concerning sampling and analysis. Nalco Environmental Sciences **161**

Mapmaking. Brochure describes a comprehensive study, "Computer Cartography: Worldwide Technology and Markets." Applications for such technology, including land use, oil pipelines, consulting engineering, and research are listed. International Technology Marketing **162**

Automotive testing. Brochure, "Testing," describes company's testing services for performance, fuel use, emission controls, and meeting federal and state certification requirements. Automotive Research Associates, Inc. **163**

Liquid chromatography. Catalog lists equipment for liquid chromatographic analysis, and discusses how to select resins, and to understand fully the liquid chromatographic process. Hamilton Co. **164**

Cyanide bath filtering. Bulletin 852 tells how large volumes of viscous, corrosive cyanide plating solutions can be filtered and recirculated with an instant start-up and leakproof operation. Sethco Mfg. Corp. **165**

Digester cleaning. Case history tells how a contractor cleaned a series of digester tanks for New York City. New techniques are compared with those of 10 yrs ago. National Power Rodding Corp. **166**

Bio-filtration. Bulletin KL4230 describes activated bio-filtration, a wastewater treatment process with both fixed film and suspended biological systems for secondary treatment. Cost advantages are discussed. Neptune Microfloc, Inc. **167**

Filter screens. Technical Bulletin 101 describes AQUA-GUARD self-cleaning filter screens. Available dimensions and mesh sizes are listed. Dyneco, Inc. **168**

Oil removal. Brochure describes Cata-Sep systems for removing oil from water in a wide variety of marine and industrial applications. MAPCO Inc. **169**

Woodwaste handling. Bulletin 6045 tells how to handle sawdust and other woodwaste for use in dual-fueled boilers properly, and tells why certain handling techniques are critical. Koppers Co., Inc. **170**

Chemical feed. Bulletin CP-103-76 illustrates and describes complete line of packaged chemical feeding systems for water treating and chemicals processing applications. Neptune Chemical Pump Co. **171**

Waste compaction. Catalog lists hydraulic material handling and waste compaction equipment for industrial, commercial, and institutional applications. Featured is the "Tubar" line. UHRDEN, Inc. **172**

Respiratory hazards. Booklet, "Basic Elements of Respiratory Protection," describes hazards, hazard assessment and control, and selection of the proper device to combat each hazard. Mine Safety Appliances Co. **173**

Ocean resources. Bibliographies cover ocean fisheries, pollution, vessels, and physical and biological oceanography. UNIPUB **174**

Sample collection. Literature describes Siemens Programmable Fraction Collector for automatic liquid chromatography. Equipment can draw up to 20 ml of a pure component. ES Industries **175**

Gas chromatographs. Publication 5952-5701 describes the 5700 Series gas chromatographs for chemical analysis, which can handle most laboratory needs. Hewlett-Packard **176**

Separation. Bulletin 482-1 describes a complete line of synthetic flocculants designed to improve solids/liquids separation. Specific product information is provided, and company personnel services are offered. Zimmite Corp. **177**

Aerated lagoons. Bulletin 311 provides tables showing sizes of aerated lagoons needed for domestic waste treatment for populations of 180–45 000. Data on how to achieve secondary BOD reduction of 85% and tertiary BOD reduction of up to 90–95+% are given. Hinde Engineering Co. **178**

Dust collectors. Brochure describes line of single, twin, and quad cyclones for industrial dust collection. Catalyst recovery, pelletizing operations, and cement manufacture are among applications listed. Emtrol Corp. **179**

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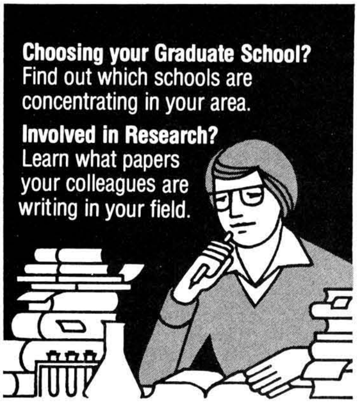

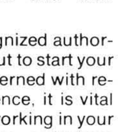

Demineralization. Two brochures describe unique packaged electrodialysis plants for water demineralization for needs up to 105 000 gpd with feed water of 100–10 000 ppm total dissolved solids. Ionics, Inc. **180**

Better oil burning. Product bulletin tells how to improve combustion of residual fuel oil with an additive—1 gal of additive for 4500–7000 gal of fuel oil. Fuel is saved and air pollution is reduced. Alken Murray Corp. **181**

Chlorination. Bulletin 4520-1 describes the ADVANCE Series 520 dual-compartment chlorination and instruments house that meets the requirements of most states for chlorination equipment. Capital Controls Co. **182**

Oxygenation. Bulletin 8000-A tells how and why pure oxygen is very beneficial for more complete wastewater treatment. Treatment in open tanks is described. FMC Corp. **183**

Waste treatment. Bulletin No. 11-694 describes modular secondary wastewater plant systems that can be put together in the field. They can have advanced treatment facilities added, and can handle even more than 5 million gpd. Licensees are listed. Marlof, Inc. **184**

Tramp oil removal. Separator reduces tramp oil content of coolants, quench water, and wash water by more than 99% with no physical or chemical effect on the separated liquids. Hyde Products, Inc. **185**

Filtration. Four data sheets feature specifications and performance benefits of dry filtration products made from combinations of various synthetic fibers and glass. Globe Albany Corp. **186**

"Viewpoints." Catalog, "Viewpoints," appearing bi-monthly gives company's line of instruments, supplies, and equipment for many different phases of environmental control, including air, water, solid waste, and noise. Horizon Ecology Co. **187**

Industrial fans. Bulletins B-5534 and B-4534 describe industrial fans for heavy-duty applications that are well-adapted to wet scrubber installations. American-Standard **188**

Laboratory Equipment. Catalog lists whole line of laboratory equipment for many different applications. Ace Scientific Supply Co., Inc. **189**

Atmosphere profiling. "ON-LOCATION" lists atmospheric profiling equipment and software for environmental, meteorological, and navigational data acquisition and processing. Beukers Laboratories, Inc. **190**

Efficient burning. Brochure describes venturi-register low-excess-air burner for oil and gas. Boiler-control functions are described. CEA Combustion, Inc. **191**

Electrostatic precipitators. Booklet provides a guide to effective ductwork design for electrostatic precipitators, and tells how this can be done without a model study. Environmental Elements Corp. **192**

Smoother solids flow. Technical paper tells how flow stoppage of dry particulate matter can be eliminated. Vibra Screw Inc. **193**

Laboratory equipment. Catalog lists a variety of laboratory equipment for many chemical, biological, and biochemical applications. Laboratory Supplies Co., Inc. **194**

Coke-pushing emission control. Brochure outlines benefits of the Hooded Quench Car System for capture and cleaning of fumes emitted during coke-pushing operations. Chemico Air Pollution Control **195**

Nuclear power. One-page explanations of waste disposal, insurance, and emergency core cooling systems. American Nuclear Society, Los Angeles Section, Box 5283, Hacienda Heights, CA 91745 (write direct).

Food from straw? It is not impossible, according to the first issue of the Danish Journal. Danish Information Office, Royal Danish Consulate General, 280 Park Ave., New York, NY 10017 (write direct).

Environmental research. API Publication No. 4275 is a status report on 42 projects complete or underway. Publications and Distribution Section, American Petroleum Institute, 2101 L St., N.W., Washington, DC 20037 (write direct).

Landfill leachate data. "Gas and Leachate from Landfills". EPA-600/9-76-004. Robert Landreth, Municipal Environmental Research Laboratory, ORD, USEPA, Cincinnati, OH 45268 (write direct).

Recycling. "The Recycler in America" is a Bicentennial brochure. John R. McBride, National Association of Recycling Industries, Inc., 330 Madison Ave., New York, NY 10017 (write direct).

Scrap resources. 16-mm film, "Scrap: The Supernatural Resource", is available for free loan, and explains the advantages of scrap use. Modern Talking Picture Service, 2323 New Hyde Park Road, New Hyde Park, NY 11040 (write direct).

Coal and petroleum analysis. Manual, "Coal & Petroleum Analysis by Atomic Absorption" has been published, and covers sampling, trace metals, and other timely topics. Bob Williams, Varian Instrument Division, 611 Hansen Way, Palo Alto, CA 94303 (write direct).

BOOKS

Land Use and the States. Robert G. Healy. xi + 233 pages. The Johns Hopkins University Press, Baltimore, MD 21218. 1976. $10, hard cover; $2.95, paper.

Congress may have failed to pass land-use laws so far, but states such as Vermont and Florida, for example, have adopted certain land-use rules. Reasons why certain states have gone this route are discussed in depth, and alternatives to state controls, and social/political/economic issues involved in land-use control are also fully covered in this work, which is a Resources for the Future Book.

Harvesting Polluted Waters. O. Devik, Ed. xi + 324 pages. Plenum Publishing Corp., 227 W. 17th St., New York, NY 10011. 1976. $29.50 hard cover.

In some cases, "polluted waters" can really mean waste heat- and nutrient-laden effluents. Perhaps such water can be used for certain aquaculture applications. This book presents papers discussing marine algae production techniques, selected organism culture, plant, mollusk and fish cultivation, and herbivore behavior. Food chains and control of unwanted organisms are also discussed.

How to Dispose of Toxic Substances and Industrial Wastes. Philip W. Powers. xiii + 497 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, NJ 07656. 1976. $48, hard cover.

Some wastes can be toxic chemical, radioactive, flammable, explosive, toxic biological, or some combination of these. Disposing of them is a tough problem as it is, and will become more so if and when toxic substances legislation passes. This book offers comprehensive state-of-the-art data on safe disposal of these kinds of wastes, and covers many industries and disposal techniques. Numerous tables, flow diagrams, and schematics are provided.

Cars, Cans, and Dumps: Solution for Rural Residuals. F. Lee Brown and A. O. Labeck. xiv + 206 pages. The Johns Hopkins University Press, Baltimore, MD 21218. 1976. $12.95, hard cover.

Tired of the dramatic impact of an automobile "graveyard" in the middle of a scenic view? Emphasizing New Mexico, this study examines the problem of large- and small-scale litter in rural areas—a problem that has previously received little attention—and discusses alternatives to this solid waste problem and economic or institutional conditions that can prevent or enhance its resolution.

Federal Environmental Laws and You. 12 pages. League of Women Voters of the U.S., 1730 M St., N.W., Washington, DC 20036. 1976. $0.75.

Those who are disturbed by unsafe water, air pollution alerts, industrial wastes, and the like, are often heard to say, "There ought to be a law!" Maybe there is a law. This booklet explains what laws exist to fight environmental degradation, and how they are applied. Order No. 564.

Introduction to Energy Technology. Marion L. Shepard et al. ix + 300 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, MI 48106. 1976. $12.50, hard cover.

Like it or not, the era of cheap, abundant energy is fast drawing to a close. This book discusses the technology of energy and its development, as well as solutions to the energy "crisis" with minimal stress on the biosphere. Problems and potentials of fossil, nuclear, and renewable energy sources are covered.

Fueling the Future: An Environmental and Energy Primer. Richard R. Sheahan. xv + 127 pages. St. Martin's Press, 175 Fifth Ave., New York, NY 10010. 1976. $7.95, hard cover.

Where will the energy to light living rooms, for example, come from in the future? To answer this question, the author offers various alternatives from solar to tidal power, and explains what the environmental implications from each power source may be. He also gives suggestions for attempting to meet future energy needs without incurring a pollution or resource depletion bill that cannot be paid.

Water and Waste Control for the Plating Shop. Joseph B. Kushner. 186 pages. Gardner Publications, Inc., 600 Main St., Cincinnati, OH 45202. 1976. $15 (add $1 for postage and handling), hard cover.

Pollution control systems are less expensive if the volume of rinse water to be treated is less, and solution concentration is higher. The author tells how to control rinse water use, minimize dragout, and cut water cleanup costs. Recovery systems, and use of ion exchange, dialysis, osmosis, and evaporation are exhaustively discussed.

Deep Coal Mining: Waste Disposal Technology. William S. Doyle. x + 392 pages. Noyes Data Corp., Mill Road. at Grand Ave., Park Ridge, NJ 07656. 1976. $36, hard cover.

Those who are familiar with coal mining areas know the waste piles and their hazards of fires and acid drainage very well. This book, based on 19 government reports and 7 patents, describes methods of controlling and preventing this pollution. Treatment and neutralization of acid drainage, control of fires and resultant air pollution, and recovery of materials, as well as reclamation of refuse bands themselves, are discussed in detail.

The Morality of Nuclear Planning?? H. C. Dudley. ix + 114 pages. RadSafety Associates, P.O. Box 452, Hinsdale, IL 60521. 1976. $5, paper.

The genie let out of the bottle at Alamogordo, N. Mex., in 1945 won't go away or crawl back in. It presented new dangers to the world, and this book analyzes these dangers and projects limits of nuclear safety. It explains why haste must be made slowly in the increase of nuclear fission reactors.

Methods in Plant Ecology. S. B. Chapman, Ed. viii + 536 pages. Halsted Press, 605 Third Ave., New York, NY 10016. 1976. $29.50, hard cover.

This book is aimed primarily at the graduate student. It covers vegetation in general, plant production ecology, sites and soils, climatology, environmental measurement, data collection systems, and other relevant topics.

Wind Machines. Frank R. Eldridge. 77 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. 1976. $2.25, paper.

This colorful book describes how wind has been used for power from antiquity to the present, and discusses the future potential for their use. Of interest to laymen and engineers, it also provides a bibliography and a list of commercial suppliers of wind energy equipment. Wind-generated power for public consumption is also discussed.

Fine Particles: Aerosol Generation, Measurement, Sampling, and Analysis. Benjamin Y. H. Liu. 845 pages. Academic Press, Inc., 111 Fifth Ave., New York, NY 10003. 1976. $34.50, hard cover.

Many of the papers presented in this book originated from the proceedings of the Symposium on Fine Particles, held at Minneapolis, Minn., in May 1975. The state-of-the-art and recent developments in instrumentation and experimental techniques are reviewed. Insight into aerosol studies for pollution control, industrial hygiene, mining safety, and fire detection is given.

Sensors for Continuous Monitoring of Toxic Ions, Nutrients, and Dissolved Gases in Water. Mark S. Shuman and Wavell W. Fogleman. xii + 122 pages. Water Resources Research Institute of the University of North Carolina, 124 Riddick Bldg., North Carolina State Universtiy, Raleigh, NC 27607. 1976. $4, paper.

This work discusses the latest in ion-selective electrodes, and a new dissolved gas sensor based on piezoelectric crystals, and their advantages and constraints. Complete technical data are given.

The Health Hazards of Not Going Nuclear. Petr Beckmann. 190 pages. Golem Press, Box 1342, Boulder, CO 80302. 1976. $10.95, hard cover; $5.95, paper.

The author discusses non-nuclear hazards in detail (*ES&T,* May 1976, p 418). For example, he shows why nuclear capacity saves 800–4000 American lives from fossil fuel dangers (explosions, fires, air pollution, industrial diseases). He also explains why each year of nuclear delay costs 20–100 lives, and why fossil-fuel or hydropower accidents are more horrendous than a nuclear accident. He also presents the case that the amount of nuclear wastes are actually small, and their disposal easy, and that sabotage and terrorism are not worrisome factors.

1976 Annual Book of ASTM Standards on Water. 976 pages. American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103. 1976. $31, hard cover.

This book is Part 31 of the 1976 Annual Book of ASTM Standards, and contains all of the ASTM standards on water analysis. Of 131 standards in the book, 15% are new, revised, or changed in status since the 1975 edition. Among new standards are infrared analysis of waterborne oils; test for radium-226 in water; and test for chlorinated phenoxy acid herbicides in water. Fifty-six of the standards are approved by ANSI. Ask for Publication Code No. 01-031076-16.

Legal Decisions in Air Pollution Control. 72 pages. Publications Dept., Air Pollution Control Association, 4400 Fifth Ave., Pittsburgh, PA 15213. 1976. $6; $4.50 for APCA members. Add $3 if hard cover is desired.

This publication is an indexed collection of legal briefs that H. Newcomb Morse has been writing for the Journal of APCA since April 1973. It covers administrative/judicial authority, expert witnesses, class actions, open burning power plants, coke ovens, and many other air pollution sources, controversies, and litigations.

Proceedings of the Conference on Environmental Aspects of Chemical Use in Printing Operations (Books, *ES&T,* July 1976, p 710) was erroneously listed as National Technical Information Service (NTIS) accession No. PB 251 401/AS. It should have read, "NTIS accession No. PB-251 406/AS.

Recommended Environments for Standards Laboratories. 20 pages. Publications Dept., Instrument Society of America, 400 Stanwix St., Pittsburgh, PA 15222. 1976. $5; $3 for ISA members.

Levels of standardization for acoustic noise, dust particle count, lighting, vibration, voltage regulation, and other factors relating to laboratories for instrument calibration are covered. Reference material is provided, and guidelines for establishing consistent environmental factors are given. Ask for ISA RP52.1-1975.

Water, Sewerless Toilets, and Gray Water System. 16 pages. Bio-Utility Systems, Inc., Box 135, Narberth, PA 19072. 1976. $2.

This publication is a treatise on those subjects.

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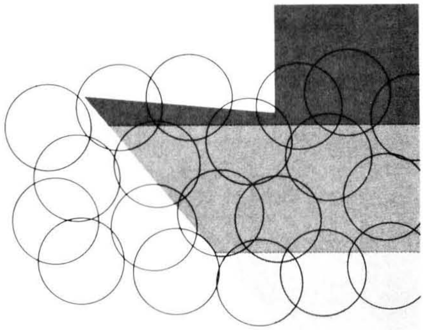

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MEETING GUIDE

September 20–24 Gaithersburg, Md.
Symposium on Methods and Standards for Environmental Measurement. National Bureau of Standards

Write: R. B. Johnson, Materials Bldg., Room B 348, National Bureau of Standards, Washington, D.C. 20234

September 21–22 Chicago, Ill.
Energy Management in Buildings. New York University's School of Continuing Education

Write: Ms. Heidi E. Kaplan, Information Services Manager, Dept. 14NR, New York Management Center, 360 Lexington Ave., New York, N.Y. 10017

September 21–23 Richland, Wash.
Second International Meeting on the Technology of Controlled Nuclear Fusion. American Nuclear Society

Write: Robert G. Clark, publicity chairman, P.O. Box 941, Richland, Wash. 99352

September 21–24 Philadelphia, Pa.
Radiological Monitoring in the Environment of Nuclear Power Facilities. Radiation Management Corp.

Write: Dr. Abraham S. Goldin, Radiation Management Corp., 3508 Market St., Philadelphia, Pa. 19104

September 25–30 Las Vegas, Nev.
1976 International Public Works Congress and Equipment Show. American Public Works Association (APWA)

Environmental topics are included. *Write:* APWA, 1313 E. 60th St., Chicago, Ill. 60637

September 26–29 Chicago, Ill.
50th Annual Fall Meeting. American Oil Chemists' Society (AOCS)

Environmental topics are included. *Write:* AOCS, 508 S. Sixth St., Champaign, Ill. 61820

September 27–29 New York, N.Y.
Conference on Aquatic Pollutants and Biological Effects with Emphasis on Neoplasia. The New York Academy of Sciences

Write: Conference Dept., The New York Academy of Sciences, 2 East 63rd St., New York, N.Y. 10021

September 27–29 Richland, Wash.
The Sixteenth Annual Hanford Biology Symposium. Energy Research and Development Administration and Battelle Memorial Institute/Pacific Northwest Laboratories

The effects of inhaled pollutants on lung tissue will be discussed. *Write:* Mrs. Judith A. Rising, symposium secretary, Biology Dept., Battelle-Northwest, Richland, Wash. 99352

September 29–30 Chattanooga, Tenn.
Fundamentals of Industrial Toxicology. The American Industrial Hygiene Association (AIHA)

Write: AIHA, 66 South Miller Rd., Akron, Ohio 44313

October 2–4 The Woodlands, Tex.
Alternatives to Growth '77. The Club of Rome, University of Houston, and Mitchell Energy & Development Corp.

Write: Jon Conlon, Mitchell Energy & Development Corp., 3900 One Shell Plaza, Houston, Tex. 77002

October 3–6 New Orleans, La.
51st Annual Meeting. Society of Petroleum Engineers of AIME

Theme is "Synergy for Recovery." *Write:* Society of Petroleum Engineers of AIME, 6200 North Central Expressway, Dallas, Tex. 75206

October 3–7 Tucson, Ariz.
The Waste Management Symposium '76. University of Arizona, Arizona Atomic Energy Commission and the Western Interstate Nuclear Board

Write: Roy G. Post, Dept. of Nuclear Engineering, University of Arizona, Tucson, Ariz. 85721

October 3–8 Minneapolis, Minn.
Water Pollution Control Federation Conference. Water Pollution Control Federation (WPCF)

Write: Robert A. Canham, WPCF, 3900 Wisconsin Ave., N.W., Washington, D.C. 20016

October 5–7 Cincinnati, Ohio
Fourth National Conference on Energy and the Environment. American Institute of Chemical Engineers and the Air Pollution Control Association (APCA)

Write: APCA, 4400 Fifth Ave., Pittsburgh, Pa. 15213

October 6–7 West Lafayette, Ind.
The Industrial Fuel Conference. Purdue University, the National Coal Association and others

Energy conversion and waste disposal in industrial utilities will be discussed. *Write:* Prof. F. M. Emshousen, Michael Golden Laboratories, Purdue University, West Lafayette, Ind. 47907

October 11–13 Denver, Colo.
ASTM Committee E-33 on Environmental Acoustics. American Society for Testing and Materials (ASTM)

Write: ASTM, 1916 Race St., Philadelphia, Pa. 19103

October 11–14 Houston. Tex.
LSA-76: International Conference and Exhibit. Instrument Society of America (ISA)

Environmental topics will be included. *Write:* ISA, 400 Stanwix St., Pittsburgh, Pa. 15222

October 12–14 Gatlinburg, Tenn.
20th Annual Conference on Analytical Chemistry in Energy and Environmental Technology. Oak Ridge National Laboratory (ORNL)

Write: L. J. Brady, Analytical Chemistry Division, ORNL, Oak Ridge, Tenn. 37830

October 12–14 Rolla, Mo.
3rd Annual UMR-MEC Conference on Energy. University of Missouri–Rolla and the Governor's Missouri Energy Council

Environmental issues will be discussed. *Write:* Dr. J. Derald Morgan, conference director, Prof. of Electrical Engineering, University of Missouri–Rolla, Rolla, Mo. 65401

October 13–15 Columbus, Ohio
Fuels from Sugar Crops. Battelle Columbus Laboratories

Write: Dr. Richard Nathan, Battelle Columbus Laboratories, Room 7224, 505 King Ave., Columbus, Ohio 43201

October 14–15 Clemson, S.C.
12th Annual Air and Water Pollution Control Seminar. Clemson University and the South Carolina Dept. of Health and Environmental Control

Write: Continuing Engineering Education, Clemson University, Clemson, S.C. 29631

October 17–22 Oxford, Ohio
Disposal of Flue Gas Desulfurization Sludges. Engineering Foundation

Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

October 18–21 Washington, D.C.
90th Annual Meeting. Association of Official Analytical Chemists (AOAC)

Environmental issues will be included. *Write:* L. G. Ensminger, executive secretary, AOAC, Box 540, Benjamin Franklin Station, Washington, D.C. 20044

October 19–21 Louisville, Ky.
Third NCA/BCR Coal Conference and Exposition. National Coal Association (NCA) and the Bituminous Coal Research, Inc. (BCR)

Write: BCR, 350 Hochberg Rd., Monroeville, Pa. 15146

Courses

September 21–22 Chicago, Ill.
Energy Management in Buildings. New York University/School of Continuing Education

Fee: $395. *Write:* School of Continuing Education New York University Registrations, New York Conference Management Center, 360 Lexington Ave., New York, N.Y. 10017

September 23–24 Madison, Wis.
Pulp and Paper Mill Sludge Management. University of Wisconsin–Extension

Fee: $125. *Write:* Robert C. Lutton, P.E., Dept. of Engineering, University of Wisconsin–Extension, 432 North Lake St., Madison, Wis. 53706

September 27–29 San Francisco, Calif.
Air Quality and Emissions Data Systems, Course No. 472. Air Pollution Training Institute (APTI)

Fee: $66. *Write:* Registrar, APTI, MD-17, Environmental Research Center, Research Triangle Park, N.C. 27711

September 27–30 Denver, Colo.
Source Sampling for Particulate Pollutants, Course No. 450. Air Pollution Training Institute (APTI)

Fee: $140. *Write:* Registrar, APTI, MD-17, Environmental Research Center, Research Triangle Park, N.C. 27711

September 27–October 1 Charleston, S.C.
Nineteenth Navy Occupational Health Workshop. Navy Environmental Health Center

No fee. *Write:* Navy Environmental Health Center, 333 Vine St., Cincinnati, Ohio 45220

October 2–December 4 Washington, D.C.
Exploring Energy Choices. The George Washington University

Fee: $255 (Saturday mornings only). *Write:* Director, Continuing Engineering Education, The George Washington University, Washington, D.C. 20052

October 4–8 Madison, Wis.
Solar Energy Thermal Processes. University of Wisconsin–Extension

Fee: $350. *Write:* Robert C. Lutton, P.E., University of Wisconsin–Extension, Engineering Dept., 432 North Lake St., Madison, Wis. 53706

(continued on page 954)

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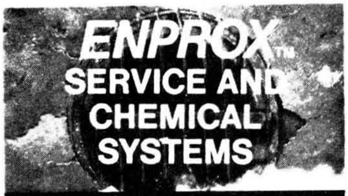

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September 30 deadline
International Conference on Advanced Treatment and Reclamation of Waste Water. International Association on Water Pollution Research (IAWPR)

Conference will be held June 13–17, 1977 at Johannesburg, South Africa. *Write:* The Technical Secretary, Reclamation Conference, National Institute for Water Research, P.O. Box 395, Pretoria 0001, Republic of South Africa

October 1 deadline
Industrial Pollution Conference. Water and Wastewater Equipment Manufacturers Association, Inc. (WWEMA)

Conference will be held April 19–21, 1977 at Atlanta, Ga. *Write:* WWEMA, 7900 Westpark Drive, Suite 304, McLean, Va. 22101

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129	130	131	132	133	134	135	136	137	138	139	140	141	142
143	144	145	146	147	148	149	150	151	152	153	154	155	156
157	158	159	160	161	162	163	164	165	166	167	168	169	170
171	172	173	174	175	176	177	178	179	180	181	182	183	184
185	186	187	188	189	190	191	192	193	194	195	196	197	198

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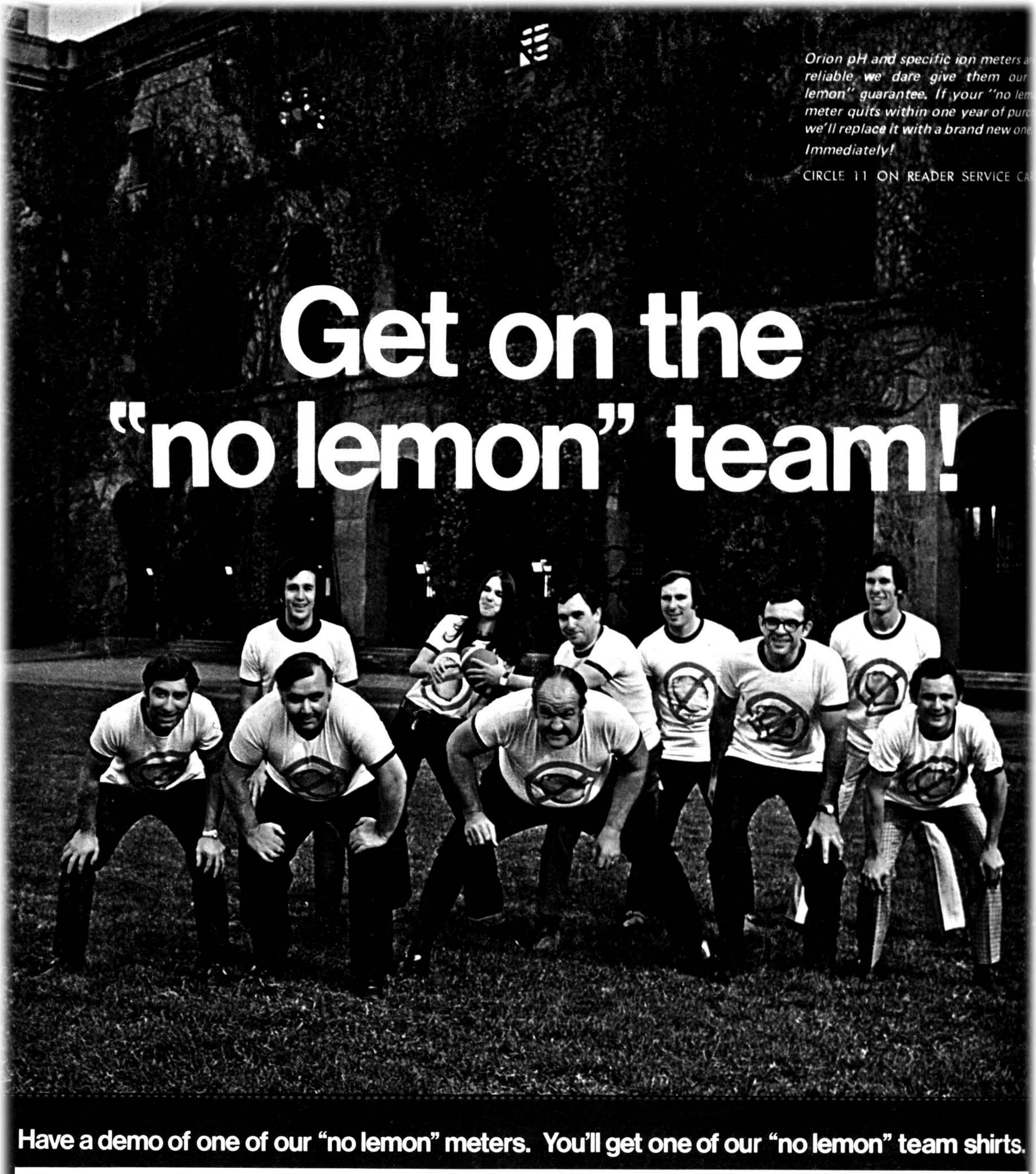

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