

Environmental

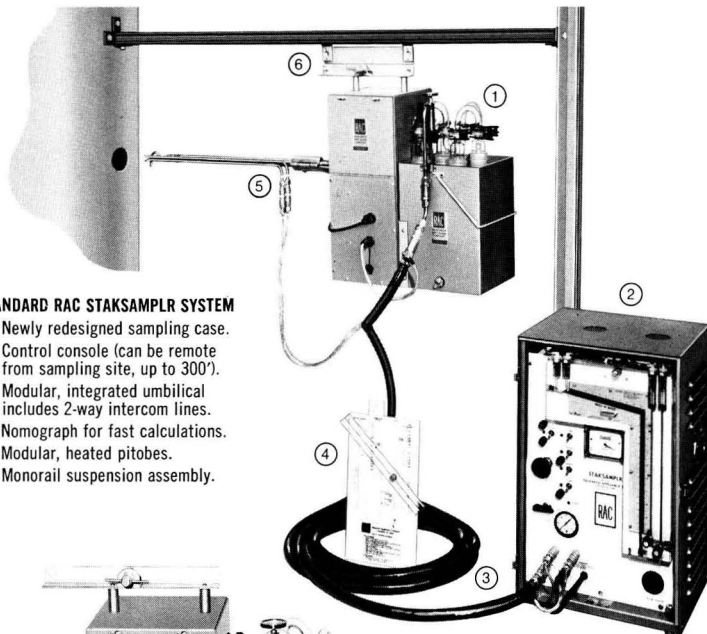
Science & Technology

AUGUST 1976

NORWAY

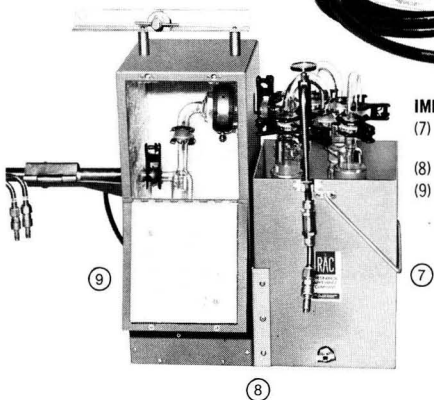


Mrs. Brundtland
Minister of the
environment 732



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- (2) Control console (can be remote from sampling site, up to 300').
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- (4) Nomograph for fast calculations.
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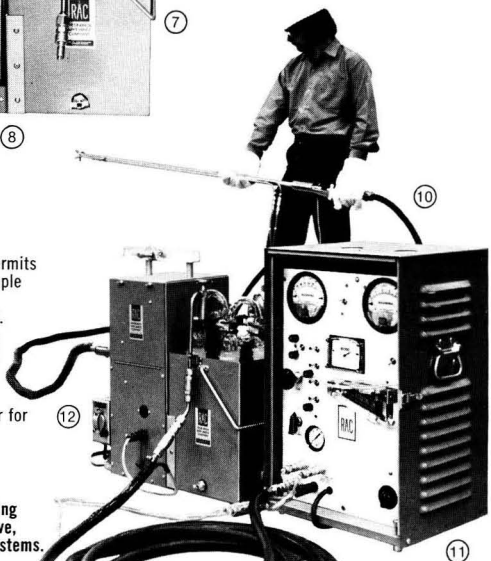
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- (8) New slip-fit interconnection.
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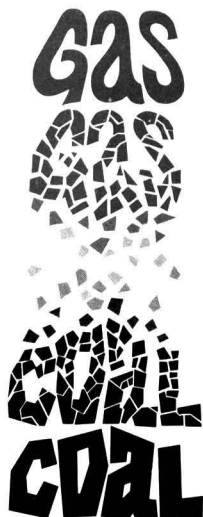
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Environmental Instruments / Laboratory Products

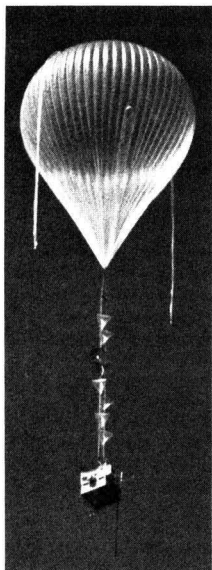
Environmental Science & Technology

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CURRENT RESEARCH

Trace organic components as fingerprints in gas chromatographic identification of spilled asphalts 761

Fred K. Kawahara

A method for analysis and identification of asphalts is developed. Perfluorobenzyl ethers as derivatives of weak acids present in trace amounts are identified by use of electron capture GC. The resulting chromatograms serve as fingerprints for identification.

Internal diffusion and reaction in biological films 765

Enrique J. LaMotta

A model for substrate diffusion and consumption in films is reported. Substrate removal is predicted to be directly proportional to film thickness up to a certain depth of substrate penetration. Resistances making observed rates less than the maximum are evaluated with the catalyst effectiveness factor model.

Chlorinated hydrocarbon pesticides in Western North Atlantic Ocean 770

Robert B. Jonas and Frederic K. Pfaender*

DDE and dieldrin are found in the North Atlantic Ocean to depths of 1000 m. Other chlorinated pesticides cannot be detected. The data show there is much variability in depth and distance from shore in the distribution of pesticides in the North Atlantic.

Lead and cadmium in dusts and soils in a small urban community 773

Robert L. Solomon* and John W. Hartford

Levels of Pb and Cd are measured in residential and nonresidential dusts of a small community. Carpet dusts from rubber-backed carpets have unexpectedly high levels of Cd. Lead in nonresidential dusts is several times greater than at residential sites. Most Pb is probably of automotive origin.

Infrared spectra of petroleum weathered naturally and under simulated conditions 777

Mark Ahmadijan, Carl D. Baer, Patricia F. Lynch, and Chris W. Brown*

Up to 60 oils are weathered in confined areas under simulated conditions by use of four weathering systems. Comparison of these results with oil from an actual spill shows that oil from three of these systems was weathered to the same extent as the oil from the spill.

Associations of chlorinated hydrocarbons with fine particles and humic substances in nearshore surficial sediments 782

Won-Wook Choi and Kenneth Y. Chen*

The levels of chlorinated hydrocarbons in sediments are related to the organic contents and to particles of 8 μm or less in size. Total organic carbons and humic and fulvic acids bear a linear relationship with concentrations of chlorinated hydrocarbons.

Long-path infrared spectroscopic investigation at ambient concentrations of the 2% neutral buffered potassium iodide method for determination of ozone 787

James N. Pitts, Jr. *, John M. McAfee, William D. Long, and Arthur M. Winer

Ambient levels of ozone are measured simultaneously by IR and the 2% NBKI impinger method. The results indicate that, depending on the relative humidity, the 2% NBKI method yields ozone concentrations 12–25% higher than the absolute spectroscopic determinations.

Corrected South Coast Air Basin oxidant data: some conclusions and implications 794

James N. Pitts, Jr. *, Jeremy L. Sprung, Minn Poe, Marian C. Carpelan, and Alan C. Lloyd

The rationale for and the results obtained by scaling existing oxidant data for Los Angeles County are presented. The scaled data show non-Los Angeles oxidant dosages lower than previously believed. Scaled down by 0.8, the new dosage is lower by 20%.

Investigation of solubilization of plutonium and americium in soil by natural humic compounds 802

Jess M. Cleveland* and Terry F. Rees

A study is made to determine solubilization of Pu and Am by humic and fulvic acids. Only slight solubilization occurs, and most of the Pu and Am precipitates out in a few days because of colloid coagulation or hydrolysis. In no instance do concentrations approach drinking water limits.

Efficient collection of polycyclic organic compounds from combustion effluents 806

Peter W. Jones*, Robert D. Giammar, Paul E. Strup, and Thomas B. Stanford

A method for collection of combustion effluents by use of a solid polymeric adsorbent is described. It is more efficient than impinger methods and gives quantitative collection of polycyclic organic compounds. This sampling system may be used at any temperature and appears to be unaffected by sulfur oxides.

Detection of vinyl chloride and related compounds by a gas chromatographic, chemiluminescence technique 810

William A. McClenny*, Barry E. Martin, Ralph E. Baumgardner, Jr., Robert K. Stevens, and Andrew E. O'Keefe

A new measurement technique is presented for vinyl chloride. The vinyl chloride is separated from other gases by GC and detected by the chemiluminescence from its reaction with ozone. A linear response is obtained at the ppm level. Sensitivity is sufficient to meet recently established standards.

NOTES

Feasibility of oil slick removal from seawater using power lasers 814

Elmar Laisk

A CO₂ laser is used to study conditions for evaporation, decomposition, and burning of oil from water. Beam intensities required for decomposition are about 25 times greater than for evaporation. It is projected that a shipboard laser with greater than 25% efficiency may be competitive with filter and foam separators.

Preparation of homogeneous dust sample for comparison of analytical results of atmospheric samples 815

Yoshikazu Hashimoto*, Tsunehiko Otoshi, and Kikuo Oikawa

A procedure for preparing homogeneous dust samples is proposed. Dust from an air conditioning unit is mixed to obtain the sample. This is analyzed by six laboratories by NAA, AAS, and x-ray fluorescence for 38 elements. Relative standard deviations for 16 elements are less than 25%.

Credits: 729, Photo Optik's Barry Baron; 730, ERDA's Westcott; 732, Arne Svendsen; 736 (right), Stewart's San Bernardino; 737, Photo Optik's Barry Baron; 742, ES&T's Julian Josephson; 750, ERDA; 760, North Texas State University

Cover: Arne Svendsen

* To whom correspondence should be addressed.

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

We can tell you exactly what's in your water. Down to the last measurable microcontaminant.



There's been a lot of speculation lately about possibly harmful viruses and organic compounds in drinking water. Now, with the help of the Water Management Division of The Carborundum Company, you can go beyond speculation. From one source, you can get both the highly specialized personnel and the equipment that can conclusively determine the presence—or absence—of these microcontaminants in your water or waste water.

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experienced technicians, chemists and virologists, and with equipment and laboratories expressly developed for this single purpose.

Our field technicians are expert in the demanding tasks of taking and preparing proper samples and shipping them correctly to our labs. To take samples for viruses, they use the Aquella™ virus concentrator. A product of Carborundum's pioneering research, it's the only detector of its kind. They take as many types of samples under as many different conditions, in as many locations and for as long as necessary, to give you reliable, comprehensive results.

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If you're ready to go beyond speculation and if you're looking for conclusive evidence of what your water does or does not contain, call or write Carborundum. Ask for further information on full-service water monitoring or, alternatively, equipment leasing with training provided.

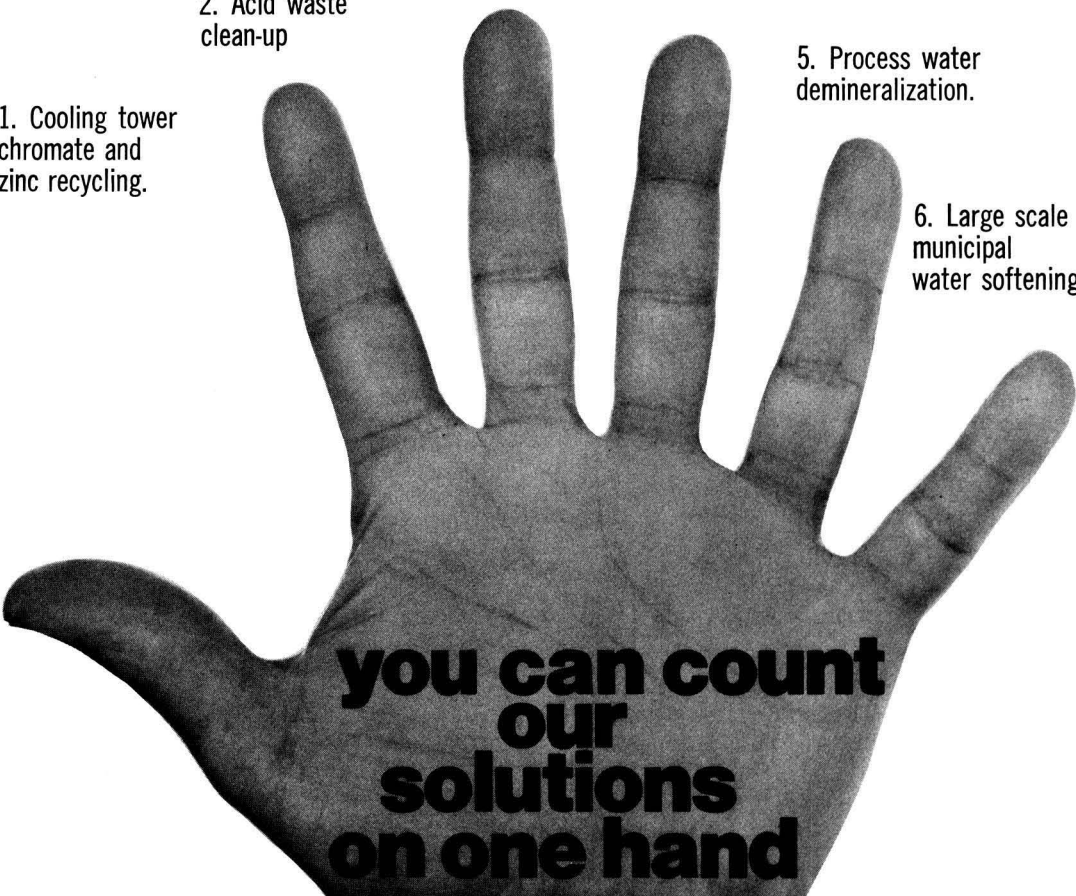
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For author's guide and editorial policy, see June
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Training needs

The decision of the Office of Management and Budget to phase out federal support of university graduate training programs rests on two beliefs: (a) that substantial progress has already been made with the establishment of professional programs at universities from earlier federal investment—and universities should guarantee their continuation; and (b) that market forces are currently the best means of fulfilling manpower needs, as present salaries in the environmental field are sufficiently competitive to attract graduates from traditional science and engineering programs. EPA, OMB, and university program advocates agree that because of the stimulus of recent federal legislation, the demand for large numbers of trained personnel will continue. The magnitude of this demand has been estimated at 5000 new specialist professionals per year for the water and air pollution control fields alone.

The federal position is misguided in several ways. First, it is not the primary responsibility of universities in this country to meet short-term national need. Rather, that function belongs to government and it is properly discharged through the use of federal research and training resources as incentives to university productivity. Second, an unfortunate corollary of the federal emphasis on the market process is that no special training is required for entrance into the environmental field. Since the phase-out decision was reached in 1973, a series of individuals and professional organizations have advised EPA and OMB that the consequences would likely be felt first in the form of decreased enrollment. This prediction has been realized as the current new MS-level enrollments in pollution control programs are approximately one-fifth of the 1973 levels. OMB's response to this observation has been to point out that the decline in non-subsidized enrollments has exceeded the decrease in subsidized enrollments; an incredible denial of the original program objective of stimulating total enrollment through partial federal subsidy.

Our federal policymakers are disregarding a paradox of their own creation; an increasing demand for professionals, coupled with increasing public expenditures for pollution control programs, and decreasing supplies of trained environmental engineers and scientists.

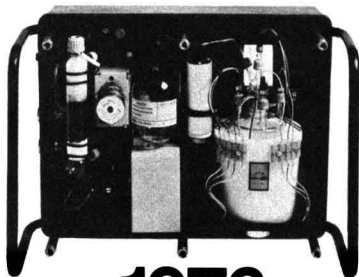


Philips SO₂ monitors: 90 days, 90%... 90 years?



1969

The first Philips SO₂ monitor is installed in the U.S.



1976

... over 60,000 data hours later this Philips SO₂ monitor is still on duty, still producing 90-95% valid data on an annual basis.

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 SO₂ monitor, Philips remains the *only* manufacturer to offer 90 day standards for unattended operation and for scheduled maintenance—no one else is even close.

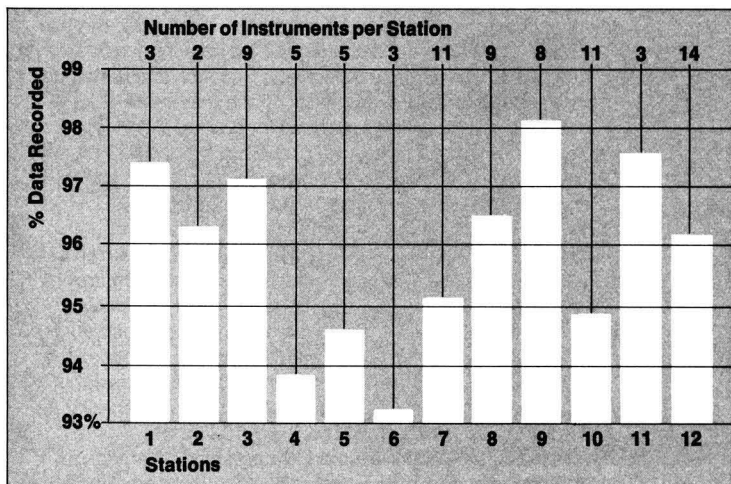
Design criteria that make the 90 day scheduled maintenance program possible include...

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



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.

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

†In the PW9755 a thermostatted SO₂ permeation source, traceable to an NBS standard, is used to provide a known amount of SO₂ 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 SO₂ 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

Philips has every reason to believe that its first U.S. monitor will be operationally effective in 1981, the year in which all monitors must be EPA equivalent. This is why equivalency for our 1969 model was important: we wanted those many companies and institutions who had purchased the PW9700 to be able to achieve the use that was originally built into this instrument . . . and this is why our present customers can be confident that in 1981 they will still be achieving 90-95% valid data on an annual basis.

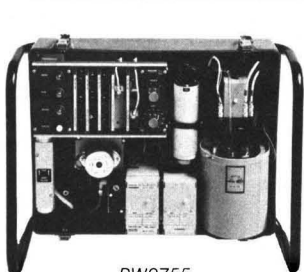


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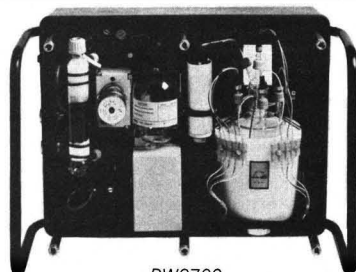
Still in use? Probably not. But as the first 90 day monitor for the control of ambient air quality, the PW9700 will have long since earned its place in history.

1976 Valid year to purchase your first (or 90th) Philips SO₂ monitor. Call us today (914-664-4500) and ask for the EQP Group (Environmental Quality Products). They'll be glad to get things moving for you.

Philips Electronic Instruments, Inc.
750 South Fulton Avenue,
Mount Vernon, New York 10550
A North American Philips Company



PW9755



PW9700



CIRCLE 16 ON READER SERVICE CARD

PHILIPS

LETTERS

Shipping wastes (correction)

Dear Sir: Oscar W. Albrecht's article "Shipping Wastes to Useful Places" (*ES&T*, May 1976, p 440) contains basic factual errors on freight rate comparisons that make his conclusions on at least two important counts misleading.

This is rather unfortunate, considering the obvious time, research and effort that went into this story. Where Mr. Albrecht erred in developing his thesis on the equity or lack of it in freight rates on competing primary and secondary materials was to cite statistics arrived at in a study by the Research Planning Institute (RPI) and Moshman Associates (Bethesda, Md.).

This study is inaccurate, at least as it relates to comparisons of freight rates on "aluminum scrap" compared with "primary ingot and pig"; and "paper waste" compared with "woodpulp". In reality, the raw materials that should have been compared for accurate freight rate appraisals are: "Aluminum scrap" and "bauxite or alumina"; "Paper Waste" and "pulpwood".

As in the case of other recyclable scrap metals, aluminum scrap, and aluminum derived from virgin ore (i.e., bauxite and alumina—Standard Transportation Commodity Code Numbers 10513, 10511) are in economic competition for use in various product markets. Ingots can be made with either virgin or scrap materials, and these ingots are *products* and cannot be compared for freight classification purposes with the raw material from which they were manufactured.

In this regard, Section 204(e) (2) of The Railroad Revitalization and Regulatory Reform Act of 1976 specifically defines the terms "virgin natural resource material" and "virgin material" to mean "previously *unused* metal or metal ore—which is or which will become—a source or raw material for commercial or industrial use."

In the aluminum industry, virgin bauxite and alumina and recyclable aluminum scrap are the competing "raw materials" from which aluminum ingot, pig, and other aluminum products are manufactured and processed.

Correspondingly, paper waste competes directly with virgin pulpwood (STCC No. 2411410) and not with woodpulp, which is a product *manufactured* from pulpwood.

Pulpwood is shipped from the forest to a paper manufacturer, who converts it into woodpulp; the fiber is then used in paper making. Similarly, paper waste is gathered, processed, and shipped to be manufactured into the pulp from which competing paper products are made. Section 204's definition of the terms

"virgin natural resource material" and "virgin material" also applies here.

Additional recognition that paper waste competes directly with pulpwood can be found in the Interstate Commerce Commission's order of April 7, 1976, Ex Parte 319 proceeding, wherein the Commission lists the competitive commodity for paper waste as pulpwood.

I am sure you can appreciate the fact that in order to have valid data regarding the issue of equity and reasonableness of current freight rates on recyclables, one has to base his analyses on comparable competing commodities.

The results of the Moshman study, unfortunately, have been repeated too often and with equally misleading results. Hopefully, this letter will help set the record straight; indeed, it is to be hoped that the facts outlined here will find a place in the reference libraries of EPA and other agencies so that the inaccuracies will not be repeated in future articles, studies, and reports.

John R. McBride

National Association of Recycling Industries, Inc.
New York, N.Y. 10017

Three R's

Dear Sir: The May issue of *ES&T* contains an excellent series of articles detailing resource recovery and reuse. Unfortunately, in the list of A/E firms active in the resource recovery field our firm, Betz Environmental Engineers, Inc. (B.E.E.) was not included. B.E.E. has excellent capabilities and is experienced in the "three R's."

Jeffrey J. Houdret

Betz Environmental Engineers, Inc.
Plymouth Meeting, Pa. 19462

Three R's

Dear Sir: I would like to congratulate you on the special articles devoted to the topic of resource recovery (*ES&T*, May 1976, pp 422-442). The resource recovery field is one with great potential for providing solutions to environmental problems and energy and materials shortages; however, it has received unfavorable coverage in recent months because of the still-developmental problems of certain large-scale facilities that have been brought on-line. *ES&T* has presented a more realistic picture.

The resource recovery industry has experienced a lull in its growth over the past year. As a contributor to the article, "The Resource Recovery Industry," and of the MITRE report prepared for EPA, I

have been closely following industry progress for several years. Since the article and report were prepared nearly a year ago, they no longer realistically represent the industry's position. The basic fact remains, of course, that the industry is looking for business opportunities; but what it has lacked to date have been some genuine successes upon which to hang its hat. The institutional and technical problems have been emphasized by the press more than the virtues and successes of industry efforts. As a result, and extra element of caution in both the public and the private sectors has prevented the industry from continuing its aggressive stance of 1974-1975. (Note the fewer number of new municipal projects that have been promoted in the past year.)

In short, the growth projections stated in the "Industry" article (*ES&T*, May 1976, p 425) now appear to be somewhat high. It will be a couple of years before each company is able to commit itself to "two new projects annually."

Progress is being made, however. The industry is using this waiting period to firm up its own positions and objectives, and out of it will come a stronger and better-understood industry. As an example, Combustion Equipment Associates and Occidental Research have now finalized the cooperative agreement that will benefit a number of resource recovery efforts. In addition, the financial community is firming up its role in the implementation process. The process may be slow but with patience and support of the Saugus and Haverhill, Massachusetts; Bridgeport and Hartford, Connecticut; Akron, Ohio, and other projects, the industry will indeed be able to offer the solutions it promises.

Susan A. Schneider

Arthur D. Little, Inc.
Cambridge, Mass. 02140

Three R's

Dear Sir: Your coverage of the solid waste field, particularly the coverage in the May 1976 issue, is of great interest to us. In that issue on page 426, Table 2 of the article by Chris G. Ganotis and Richard E. Hopper, a variety of companies are listed but not the name of our firm. We are presently active for the State of Connecticut solid waste and resource recovery program, and we have just completed the first phase of a similar program for the Hackensack Meadowlands Development Commission in New Jersey.

Henry Gitterman

Burns and Roe Industrial Services Corp.
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Why we're running our 1976 Pollution Show in the Sierra Club's backyard.

No state has made a greater effort to preserve the quality of the environment than has California. They've done more than discuss the problems of air, water, noise and solid waste pollution. They've taken steps to solve them.

That's why we chose the Anaheim Convention Center for this year's Pollution Engineering Exposition & Congress, to be held in November.

California: Land of tough pollution laws.

Anaheim is in the center of the country's biggest pollution control market. California and its neighboring states have the most stringent anti-pollution legislation in the country.

Thus you'll be able to see hundreds of pollution control products that are being used to meet many of these rigid standards.

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.

California: Land of beautiful places to visit.

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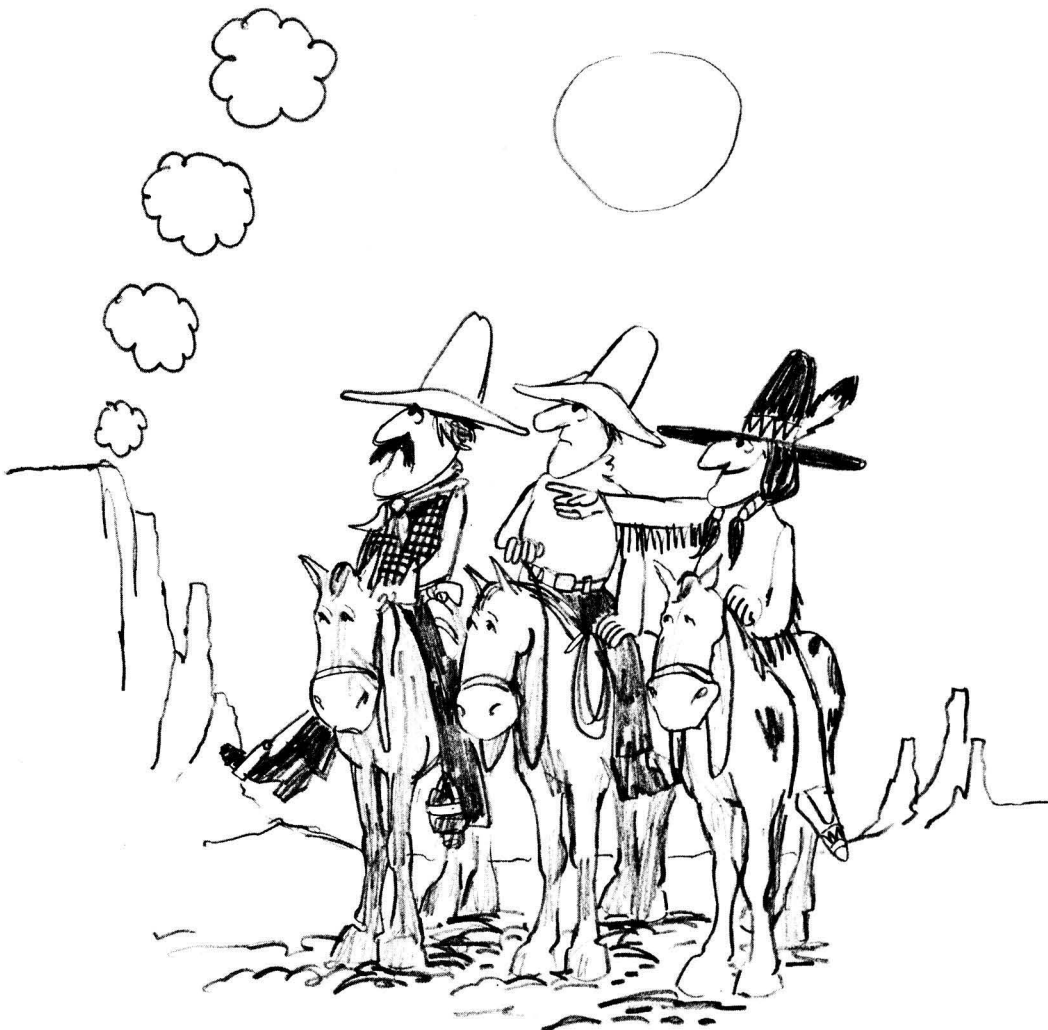
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To meet this need, Intertech is introducing the Model D-R 110 Optical Transmissometer. Mounted on-stack, the D-R 110 forms the heart of an automatic, unattended Emission Measuring System—a system that gives continuous, repeatable, highly accurate results. Output is linear with opacity or optical density and can be fed either to a

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The Transmissometer works on the photoelectric dual-beam principle—where a light beam is transmitted across the stack, reflected back, and then “nulled” against a reference signal. The design and equipment have been widely used in Europe where stringent stack emission controls have long been in force.

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CURRENTS

INTERNATIONAL

A water quality data storage and retrieval system for the Nile River and Lake Nasser, Egypt, is being developed in a cooperative effort between the Egyptian Academy of Scientific Research and Technology and the University of Michigan. Using the experience of the U.S.' STORET system, Canada's NAQUADAT system, and Sweden's CEIS system, the developers are designing a prototype system that can be implemented on a medium-size computer system and can be used by developing riparian countries.

Sweden has received recommendations on SO_x reduction from a Ministry of Agriculture commission. These recommendations include a phaseout of use of heavy fuel oil with more than 1% sulfur and diesel oil with more than 0.3% sulfur. Other approaches encompass mandating decreased SO_x emissions from process industries, and use of alternative energy sources that pose no sulfur problem.

WASHINGTON

EPA must release about \$136.4 million in planning grant funds for areawide waste treatment management. These funds must remain available through September 30, 1977, according to the U.S. District Court for the District of Columbia's ruling in *National Association of Regional Councils v. Train*. The court also ordered EPA to promulgate by this September 30, new regulations or amendments to existing regulations needed to implement the terms of the order.

EPA administrator Russell Train has reversed his February 17 decision to ban mercury in water-based paints and coatings. The reversal was based on evidence that non-mercurial substitutes for bactericides and fungicides in water-based paints and coatings were inadequate and ineffective. The ban on mercury in other paints, seed treatments, and turf and golf course applications remains intact.

CEQ recently concluded that the environmental impact statement required by NEPA is working well. The Council on Environmental Quality stated that some administrative adjustments



CEQ chairman Peterson

are needed, but no legislative corrections to the National Environmental Policy Act of 1969 are required. Russell Peterson, CEQ chairman, stated that "The improvement most critically needed is to make the EIS process more useful to, and more a part of, agency planning and decision-making." The report concluded that the EIS process did not result in needless delays as agencies are improving their environmental expertise and preparing the EIS's earlier in the decision-making process.

Taking the environmental impact statement to its absurd limits, the NIH will undertake an assessment of an unknown quantity. With the issuance of guidelines for the conduct of NIH-supported experiments involving recombinant DNA molecules—the test-tube combination of genetic information from different organisms—Dr. D. S. Fredrickson, director of the National Institutes of Health, stated that the institute would assess the impact of these guidelines in accordance with the NEPA (1969). A draft EIS is to be completed by September 1.

The Supreme Court has decided that state air pollution control plans approved by EPA cannot be challenged in federal court on the grounds that meeting them is not technologically or economically feasible. According to the decision, industries should settle their problems with the state in the formulation of state implementation plan.

The Small Business Administration is now empowered to guarantee pollution control bonds. Under the amendment to

the Small Business Act, the SBA provides 100% guarantees for tax-free municipal bonds, guarantees that make these bonds attractive to investors. Under the new program, small business industrial revenue bonds (IRB) will be grouped in packages to make them attractive to underwriters. State and local government authorities empowered to issue IRBs will float the loans whose proceeds will be used to purchase pollution control facilities. These facilities will then be leased to small businesses; lease payments will be used to pay principal and interest on the SBA-guaranteed bonds. This guarantee program may provide \$100 million during the first year and \$700 million during the fifth.

STATES

By the end of the year, nearly pollution-free cars will go on sale in California. Volvo has developed this automobile that uses an American-made three-way catalytic converter. This smog-free auto is said to get 10% better mileage than current models. The new catalytic system, designed by Engelhard Industries (Edison, N.J.), works with present internal combustion engines. On a per mile basis, these new Volvo cars average 0.2 g hydrocarbon, 2.8 g carbon monoxide and 0.17 g NO_x. These values are well below federal standards and are even better than newly adopted California standards.

Muskegon County, Michigan's 42-mgd land treatment system's 2-yr operating and maintenance performance was reviewed; start-up problems were overcome and operating costs were reduced and revenues from crops were increased. This county managed system recycles wastewater nutrients for irrigation of 5000 acres of corn-growing farmland. Operating costs were less than that predicted by the EPA for land treatment costs and lower than typical costs to achieve the same degree of treatment by other types of processes. Net operating and maintenance costs for 1976 are expected to be 59% more per gallon treated than 1975 costs because of higher electric rates.

Beaches in Nassau and Suffolk Counties, N.Y., were plagued by floating grease and tar globules, waste

plastic, charred wood, old vegetables and their crates, and other undesirable materials. The grease and tar had a high fecal coliform count—in millions/100 ml. However, sewage sludge dumped at the designated New York Bight sites (*ES&T*, June 1976, p 530) did not appear to be among the items washed up onto the beaches. NOAA and county spokesmen speculated that these materials may have come from the Hudson River and Raritan Bay; they noted that a Nassau County sewage plant exploded on June 2. They also noted that a southwest wind had been blowing the beaches for 3 weeks; the wind carried drift bottles in the same direction the solid waste traveled.

Minnesota's Gov. Wendell R. Anderson signed into law legislation limiting the sale and use of PCBs after January 1, 1978. However, if no suitable substitute is available for polychlorinated biphenyls for a particular product, then the state Pollution Control Agency must issue a certificate of exemption delineating the permitted use, sale or purchase of PCB or a PCB product. Under the new law, products containing PCBs must be labeled conspicuously after July 1, 1977.



Minnesota governor Anderson

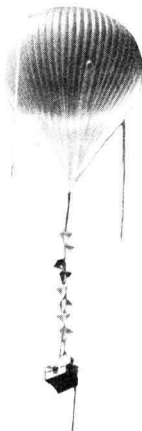
The District of Columbia surveyed the public's response to its air pollution episode of last year (July 29–August 5, 1975). The random sample included 1500 people who work in D.C., but lived in D.C. (42%), Md. (32%), and Va. (26%). During the episode 81% of the respondents commuted by bus (38%) and private car (33%) three days or more during the episode; another 9% commuted less than three days and the remaining 10% did not commute at all. Of this last percentage only 8% (12 respondents) said they remained home because of the air pollution alert. The

largest part, 57% (90 respondents), said they were on vacation.

Residents near the Hanford (Washington) nuclear reactor are exposed to twice the amount of iodine-132 as are residents of the Pullman-Spokane area, some distance from the Hanford area. Iodine-132, a decay product of volatile tellurium-132 formed during the fission of uranium, is particularly hazardous because it can be concentrated in the thyroid gland. The dose of radiation received by the thyroid was estimated to be 0.1 rem over a three-month period at Pullman, according to Washington State University scientists; over an extended period of time this would translate to about four excess thyroid carcinomas per year.

MONITORING

One way to keep tabs on urban air pollutants, especially SO_x and automobile emissions, is by following them aloft in a heavily instrumented balloon, such as Da Vinci II. The balloon was launched from Arrowhead Airport, west of St. Louis, Mo., on the morning of June 8, stayed over St. Louis for most of the day, and was carried at night to where it landed the next morning, near Griffin, Ind. Scientists manning the balloon found how pollutants from St. Louis industrial and urban sources were trapped in an air inversion by day, and were carried by above-ground night winds, with very little dilution, all the way across southern Illinois, in effect, traveling with the balloon. Generally, the balloon, whose flight was sponsored by ERDA, the EPA, and NOAA, with National Geographic Society support, was held to 1000–1500-ft altitudes.



Collecting samples for RAPS

TECHNOLOGY

Solvent vapor recovery becomes essentially 100% efficient with an activated carbon module. Carbon is regenerated, and solvent recovered with a carbon wafer water purge and low pressure live steam infection in the Dyna 3 system developed by Interdyne, Inc. (Indianapolis, Ind.). The water purge's function is to suspend and disperse the carbon prior to live steam injection. This procedure eliminates steam channeling and sharply increases energy efficiency. The water-saturated condition also eliminated bed fire possibilities. The system can be sized to specification, and assume 100% solvent recovery; oversize carbon requirements by a 50% factor to make up for regenerating inefficiency are unnecessary.

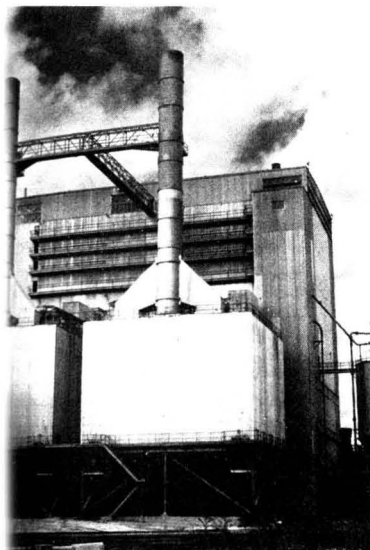
Profitable concentration of waste oil emulsions and latex wastewater was described at the Third National Conference on Complete Water Reuse by Iqbal Bansal of Union Carbide's Membrane Systems (Tarrytown, N.Y.). This concentration is accomplished through "Ucarsep" ultrafiltration. Water can be returned to cleaning baths, and the emulsified oil concentrate has a heating value of 5000–15 000 Btu/lb. Ultrafiltration also removes 80–97% water for recycle, to yield a concentrated latex. The water permeate contains only 8 ppm of suspended solids. The company estimates that net savings on a 50 000-gpd unit can run as high as \$42.59/1000 gal feed.

Separation and recovery of metals such as chromium, copper, and nickel from mixed plating plant sludges can be brought about by a chemical-treating process. Iron and zinc are also separable and recoverable, according to the Osaka (Japan) Prefectural Industrial Research Institute (OPIRI), developer of the process. With the OPIRI process, the sludges are treated with oxalic acid, then ammonia, and finally, sodium hydroxide. Bivalent copper, nickel, and zinc become insoluble oxalates; trivalent chromium and iron are extracted, and adjusted in pH. Remaining oxalates extract remaining metals as hydroxides. Chromium removal is almost complete, and its removal facilitates handling metals remaining in the sludge.

Valuable ash residues can be produced from toxic industrial wastes by a proprietary molten-salt incineration technology developed by APS Inc. (Pleasantville, N.J.). The technology can process and dispose of wastes such as

fat-hardening nickel catalysts, chemical tower bottoms, and tannery sludges. Antimony, nickel, and chromium oxide can be recovered from these residues. The principle is catalytic properties of the molten salts that allow oxidation at below 1000 °F. These low temperatures prevent volatilization of toxic metals, while allowing complete oxidation of organic matter in the residue. Also, effluent gases are scrubbed or reacted with the regenerable molten salts before release to the atmosphere.

"One of the world's cleanest pulp and paper mills" can be ascribed to twin double-chamber electrostatic precipitators that control air emissions and recover salt cake at the Cantonment, Fla., mill of St. Regis Paper Co. The precipitators were designed and fabricated by Environmental Elements Corp. (Baltimore, Md.), a subsidiary of Koppers Co., Inc. They handle exhaust gases with a dust load of 2–12 grains/scf dry, from the low-odor recovery boilers, and have double-wall, carbon steel casings to reduce corrosion. The equipment is part of a 5-yr, \$45-million air improvement program recently completed at the mill.



Precipitators on pulp mills

Possibly, stratospheric chlorine from photolyzed chlorofluorocarbons may react with NO_2 to form chlorine nitrate (ClONO_2). Mario Molina of the University of California (Irvine) told a National Bureau of Standards (NBS) photochemistry conference. If ClONO_2 is present, Molina foresees that original ozone depletion predictions might be

reduced by only 20–30%, since ozone depletion occurs mainly above 35 km where ClONO_2 is readily photolyzed. Molina also told the NBS conference that chlorofluorocarbon "sinks", such as ocean dispersal, trapping in snow, or reaction with ions, are not of importance when compared to stratospheric photolysis. However, he also said that tropospheric "sinks" cannot be ruled out.

INDUSTRY

General Motors chairman Thomas Murphy called on GM stockholders to urge their Congressman to support revised automotive emission standards proposed by Rep. John Dingell (D-Mich.). Dingell's amendments would set these standards at less stringent levels than those presently imposed for 1978. Murphy warned that if the original 1978 standards are retained, the U.S. "will experience a terrible waste of fuel," and "the introduction of alternative engines, such as the passenger-car diesel being developed for 1978, will be precluded." He said that the cost to the car buyer would be "enormous, and all for a virtually imperceptible effect on air quality."

International Nickel (U.S.) Inc. (New York, N.Y.), the U.S. subsidiary of Inco Ltd., has formed the International Metals Reclamation Co., Inc. (INMETCO) to build a new reclamation facility that will convert specialty steelmaking waste products into commercially useful metals. Planned for operation by mid-1978 at Ellwood City, Pa., the facility will have an initial design capacity to process more than 40 000 t/yr of wastes such as flue

dust, grinding swarf, and mill scale into a nickel-chromium steel remelt alloy. R. Todd Grant has been appointed vice-president and general manager of INMETCO, which is expected to employ 100 by 1978.

F. D. Gottwald, Jr., chairman of the board of Ethyl Corp., expressed disappointment at the decision of the U.S. Supreme Court not to review the lower court's decision which upheld the EPA rules for phasedown of lead in gasoline. He said that this decision will lead to increased gasoline costs, and to the consumption of 5–6% more crude oil annually. Gottwald noted that lead antiknocks have been used for over 50 yrs, and that Ethyl has shown that there is no medical or scientific evidence to support allegations that lead antiknocks will endanger public health. However, since Ethyl anticipated the phasedown decision, it is continuing its diversification program which Gottwald expects will result in a continued growth rate of 10%/yr.

One of the most difficult problems in installing a water recycling system is separating process water from cooling water. Harold Richardson, superintendent of the power production division of U.S. Steel Corp., told the 84th General Meeting of the American Iron and Steel Institute. He said that at U.S. Steel's South Works plant near Chicago, of a 400-mgd discharge, only 35% was process water. For a complete recycle system, Richardson recommended adequate surge capacity, such as that of a lagoon, and good solids removal capacity to minimize the use of costly chemical treatment. Operating and maintenance personnel training is also very important, he said.



INMETCO's Grant

American Can Co. has completed a million-dollar program to eliminate SO_2 "blowstack" emissions from a pulping operation at its large paper mill at Green Bay, Wis. Mill manager John Fulkerson called the project "a technical breakthrough in that it is the first to eliminate the stack gas in a calcium-base sulfite mill." In the new installation, digester gases are sent to a condenser where moisture vapor—more than 97% of the gas volume—is condensed. Residual gases are reabsorbed into cooking acid used for pulpmaking. The installation's complexity and high cost came from the need to handle a large gas volume in the short time of digester blowing. Fulkerson said that the new system fully meets "best practicable" as defined by the EPA and the Wisconsin Department of Natural Resources.

INTERNATIONAL

Environmental protection in Norway

Nearly 3.5 years old, Norway's Ministry of the Environment recently presented a "White Paper" on measures against pollution that will be debated in the Norwegian Storting (Parliament)

Established in May 1973, the Royal Norwegian Ministry of the Environment has responsibility for the control of pollution and waste. It also has general responsibility for land-use planning and zoning regulations, nature conservation, and open air activities. Organizationally, within this Ministry there is a Department of Natural Resources. Affiliated with it are



Minister of the environment
Mrs. Gro Harlem Brundtland

institutes for air and water research—Norwegian Institute for Air Research (NILU) and the Norwegian Institute for Water Research (NIVA). Also within the Ministry are a number of subsidiary institutions such as the State Pollution Control Authority, which functions as the secretariat for the Smoke Control Council and the Council on Oil Pollution.

Mrs. Gro Harlem Brundtland, Minister of the Environment, reminds *ES&T* that when the various aspects of pollution and pollution control are considered, a few important facts about population, geography, and meteorology should be borne in mind. Norway covers about 325 000 km² with a population of 4 million people. About 70% of the area is above the forest limit; 25% is covered by forest, and the remaining 5% is where the people live—often in narrow bands along the valleys

and coast. The fjords stretch deep into the country. Often they have a shallow part at the entrance, which limits circulation of water.

Because of meteorological and topographical conditions, dispersion of emissions is often poor. Temperature inversions of long duration occur in the winter. Abundant supplies of hydroelectric power are the base of the country's large electro-metallurgical industry and its chemical industry. Many of the works and smelters, especially the older ones, are situated at the head or along the fjords and are surrounded by mountains. Consequently, with poor dispersion, even relatively small emissions cause problems.

The minister says that odors are another problem. The fisheries are of great importance. From 2.0–2.5 million tons of fish, 75% of the yearly catch, is converted to fish-meal and fish oil, whose production causes severe odor problems at some places along the coast.

The legal basis

Norway's main environmental laws are the Neighbours Law on air pollution (1961) and the Law on Protection against water pollution (1970). Each law instituted a permit system for new polluters—for example, air pollution starting after Jan 1, 1962 and water pollution starting after Jan 1, 1971. Permits for emissions to the air are given by the Smoke Control Council; those concerning water effluent discharges are issued by the State Pollution Control Authority (SPCA). For existing emission sources that were operating when these laws came into force, the authorities have power to set deadlines for applications for emission permits.

Another law of environmental concern is the law on restrictions on the use of fuel oil. Fuel oil restrictions are in force in Oslo and Drammen now. Here the authorities:

- can prohibit the use of fuel oil totally
- set limits on the sulfur content
- prescribe that only distillate be used.

Another law that is important from an environmental viewpoint is its law on protection against oil damage (1970). According to this law, the Council on Oil Pollution is established to direct the work in this sector.

In other laws there too are sections applicable to pollution and environmental protection. For example, the health law may be applied, as can laws concerning fisheries, traffic and motor vehicles. The building law includes sections requiring that pollution (sewage) problems be solved in connection with planning.

Since promulgation of its main laws, emission standards have been implemented for some of the industries and their equipment. For example, there are rules regulating the manufacture of road-surfacing materials and bark-burning furnaces.

Water guidelines are normally issued centrally, but for municipal sewage a certain degree of decentralization on permits is relegated to the county administration. In other words, control of sewage is decentralized whereas control of industrial effluents and emissions to air is not. Permits for industrial discharges to water are given by the SPCA; to air, by the Smoke Control Council. When minor violations occur, the violator is put under a deadline to correct the emission. More serious violators may be taken to court.

Future environmental policy:

A new comprehensive law will be presented this year:

- This law is intended to cover all aspects of pollution such as air and water pollution, solid waste of all types ranging from kitchen waste and packaging, waste paper to old cars. One of the main purposes will be to foster recycling. It is announced that trials to this end will be conducted; also the use of grants are considered.
- The new law will also cover all aspects of noise, whereas the present Neighbours Law only covers noise from industrial enterprises. A separate White Paper concerning noise will be presented.
- The polluter-pays principle will be strictly adhered to for all new enterprises, and new industrial plants must use "best applicable technology" which implies that cost also will be taken into consideration. It is also announced that a committee will be appointed to review the use of taxes

Norway:

towns and plants

In some cases, a daily fine may be imposed until the correction is made.

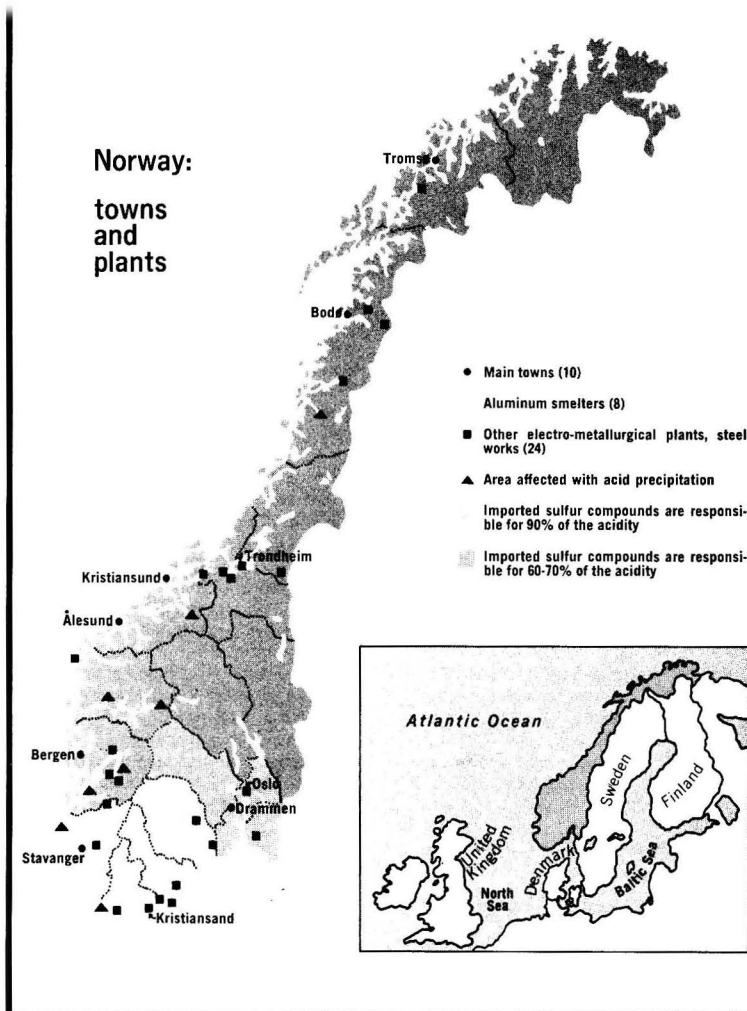
Air monitoring

Thus far, only SO₂ and particulate matter are monitored on a nationwide scale. Most stations (110 of 120) show concentrations well below the guidelines of the World Health Organization SO₂ limit of 60 µg/m³ as yearly mean and 98% of the 24-h mean below 200 µg/m³. Oslo and a few other places show values in excess of the WHO guidelines.

With regard to particulate matter, concentrations above the WHO guidelines are common, the guidelines being 40 µg/m³ as yearly mean and 98% of the 24-h mean below 140 µg/m³. Industrial emissions and road traffic are the reasons. A few locations, especially in the vicinity of metallurgical plants, have dustfalls that are viewed as too high.

Air pollution from transportation sources is not a big problem in Norway, although concentrations for lead, CO, and NO_x in excess of U.S. air quality standards are found in congested streets or along a few of the most heavily used highways.

Smog is not a problem in Norway today;



on emissions and polluting products.

- It is intended increasingly to use emission guidelines as background material when permit applications and other measures against pollution are considered.
- To date, environmental impact statements have had no formal place in the Norwegian system, although considerations of effects are made when permits are given. In the bill, the presentation of environmental impact statements will be made compulsory for new enterprises exceeding a certain size.
- Acid precipitation is a very serious problem in Norway. To help alleviate the situation, maximum sulfur content in fuel oil will be 1% for all new consumers from January 1, 1977 in the southern part of the country. Existing enterprises will get the same restrictions as from July 1, 1978.
- In the entire country, the goal is to meet the WHO guidelines for sulfur oxides.
- Emissions from gasoline-powered vehicles are in force for vehicles

registered after January 1, 1974. The standards proposed by ECE are used, and new stricter standards will be promulgated during 1977. Maximum lead content in gasoline is 0.4 g/l.

- Contingency planning against accidental spills of oil and chemicals is regarded as very important. The existing organization was recently reported on by a special committee. The organization is now incorporated in the State Pollution Control Authority, and the procurement of additional booms, chemicals and skimmers is under way.

- People in Norway are very concerned about the dangers that a blow-out in the North Sea may represent. Safety rules are under review. There is some doubt, however, that existing equipment (booms) will be able to cope with the rather severe weather conditions in the North Sea, especially in winter. R&D is going on. Norway participates actively in work going on in several international organizations like OECD, ECE, Council of Europe and UNEP, and will do the same in the future.

acid precipitation is its biggest problem. The possibility of smog in the near future is regarded as small. In 1977, however, a petrochemical complex will come on stream. It is situated a few miles from an (old) fertilizer plant. Rather strict limits are set for both plants.

Industrial emissions

Smoke from the ferro-alloys industry is a problem, and a big one. Norway's ferro-alloys industry is about 1/3 the size of the corresponding industry in the U.S. Some works are at locations where dispersion is poor.

Fluorine emissions from the country's eight aluminum smelters (total capacity 700 000 t/y) have caused damage, especially around older smelters where dispersion is poor. A special control program has been conducted since 1966. Samples of conifer needles, grass, and bones of sheep and cattle are analyzed for fluorine content. Fluorine concentrations around some smelters are too high but emissions are registered. There is no danger of human fluorosis.

The biggest odor problem in Norway comes from its fish-meal plants, although sulfate pulping gives rise to complaints. Lesser odor problems stem from coffee roasters and plastic production.

Acid precipitation is regarded as one of Norway's most serious pollution problems. Especially hard hit is a region to the northeast of Kristiansand where "imported" SO₂ and sulfates account for 90% of the acidity.

Precipitation of 5 tons of sulfates per km² has been reported, of which 60–70% is sulfuric acid. Buffering capacity in soil and water is low, and in this region fish like trout and salmon have disappeared from many watercourses. There are signs that acid precipitation also affects the whole of the southeastern part of Norway where "imported" sulfur compounds are estimated to account for 60–70% of the acid precipitation.

Water pollution

Untreated sewage, industrial effluents, and agricultural runoff represent a threat to many lakes and streams. In many cases, these effects combine with the effects of reduced waterflow caused by the development of hydroelectric power. Thus far, the oceans around Norway are not much affected by pollution; but some of its fjords, especially the inner parts, are heavily polluted, mostly by municipal sewage.

Solid waste, sludge, and oily water represent problems well known in all industrialized countries. In Norway, the situation regarding beverage bottles is good. Here, the percentage of bottles returned for reuse is between 95–98%. This return is achieved by a deposit system, combined with a tax on one way bottles and beverage cans.

Industrial cleanup

According to both the water law and the Neighbours Law (air), the authorities have set deadlines for "old enterprises" facilities existing before the passage of the laws, to apply for emission permits. Deadlines have been set for the pulp and paper industry, and electroplating and its associated industries. Time limits for the applications varied from August 31, 1971 to March 1, 1976. These deadlines have been set for the ferro-alloys industry, iron

and steel foundries; the fish-meal industry, and food-related industries including canning, slaughterhouses, and dairies. Time limits for compliance have also been set for the paint manufacture, vegetable oil production and fat hardening, explosives manufacture and the textile industry.

To date, the entire ferro-alloys industry, the fish-meal industry, and iron and steel foundries have received their emission permits, the minister says. During 1977–81, air pollution control equipment will be installed in the ferro-alloys industry, the deadline for the last furnace being July 1, 1981. In this case, care has been taken to spread installation in each individual works to minimize disruption of production. The cost is estimated to be \$110 million; the total quantity of collected dust is estimated at 110 000 tons/year. The problem of recycling this dust has not been solved, but a small part of it will be used.

This year (1976) all electroplating plants will be cleaned up. Next year, all iron and steel foundries will be controlled. Heavy metal sludges from the electroplating industry are dumped at specially prepared sites. Recycling of these sludges will come at a future time.

By midsummer 1978, all water discharges from the fish-meal industry will be controlled, and by January 1979, odorous air emissions also will be controlled. Thus far, the permits are based on seawater scrubbing of the exhaust gases from driers and the like, followed by incineration. Full-scale tests of seawater scrubbing/chemical scrubbing are going on at two plants. If deodorization is deemed to be adequate, the permits may be altered to allow the use of this method, which is expected to be considerably cheaper than incineration. At present, the cleanup cost to this industry is estimated at \$50–60 million.

For the pulp and paper industry the deadline to apply for water effluent discharge permits was August 31, 1971. To achieve reduction of the discharges from the sulfite pulp processing, this industry also needs permits for air emissions because of the burning of spent lye.

This industry has considerable structural problems and the combined processes of cleaning up and restructuring is rather time-consuming. Consequently, only part of the pulp and paper industry has so far gotten their deadlines fixed. By 1978, total discharges to water will be reduced by about two-thirds. As a consequence of the burning of spent lye a certain increase in SO₂ emissions may occur, dependent on the magnitude in switching from calcium-based to magnesium-based lyes. The cleanup cost for the pulp and paper industry is estimated at \$200 million.

Metal works

Iron and steel works have obtained their permits; cleanup will be completed in two

years (by 1978). All aluminum smelters have discharge and emission permits in conjunction with extensions of the smelters. Two of the eight smelters have emission levels of about 1 kg of total fluorine per ton of aluminum, but some potlines in other smelters have emissions of the same magnitude. Often, dispersion of these emissions is poor because of meteorological and topographical factors, and reduction of emissions is necessary. Bringing about this reduction is a slow process because complete replacement of old potlines will be necessary and the question of additional power supplies must be solved in some cases.

The biggest single source of SO₂ in Norway is a small copper smelter that emits some 20 000 tons of SO₂ a year. It is not economically feasible to install cleaning equipment at this plant. Plans are under consideration to extend the smelter to smelt the total Norwegian production of copper concentrates in which case a sulfuric acid plant will be erected.

At two other smelters (copper/nickel and zinc), progress is being realized in the reduction of heavy metal discharges to the sea, and safer dumping of the remaining sludge. By 1984, complete cleanup of the entire Norwegian metals works is expected; the first half of the program will be completed by 1977. The total cost for cleaning up industrial discharges and emissions is estimated at \$800 million.

Financial help

To help industry finance the necessary investments, special long-term loans are granted. At present, these loans cover 70% of the investment cost. Only in exceptional cases are direct grants given. Investments in cleanup equipment are also exempt from the 13% investment tax. Additional loans have been granted for investments during last winter (1975–76), both to speed up installation of cleanup equipment and to alleviate unemployment.

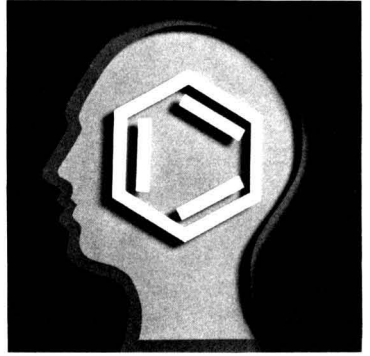
Sewage

At an earlier date, the Ministry of the Environment presented a comprehensive plan for the utilization of Norway's water resources and the improvement of municipal sewage systems and sewage works. Sewage is a big problem. Many of the sewage systems are inadequate and leaky; the efficiencies of many existing wastewater treatment plants are low because of a lack of properly trained operators. In some cases, there is the danger of eutrophication, such as with Norway's greatest lake, Lake Mjøsa, in the southeastern part of the country. These cases will be given priority, and cleanup should be complete by 1980, whereas cleanup for the whole of Norway will be complete by 1990. The cost is estimated to be \$4.5 billion. Financing will be by special loans to the municipalities, sewage taxes and, to some extent, grants.

This story was written for *ES&T* by Øystein Heen, chief of a division in the Ministry of Industry. He is also a member of the Smoke Control Council.



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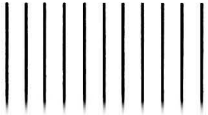
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Energy recovery from pulping wastes

Ecodyne evaporators eliminate water discharge, recover spent liquor, and increase process efficiency

The Port Angeles division of ITT Rayonier (Wash.) produces various grades of pulps, including those for ordinary paper, acetate, and viscose rayon. About 500 tons/day are produced and distributed as raw materials for manufacturers around the world.

In the past, spent sulfite liquor from the pulp mill that included other wood solubles, degraded cellulose, unreacted ammonium bisulfite and SO_2 , were discharged into the Strait of Juan de Fuca, where it was quickly dispersed by tidal action. Now, after a \$35 million mill expansion program, Rayonier is recovering materials and heat energy to improve process efficiency.

When the state of Washington established a new pollution and environmental protection code, the company first considered switching the mill to a soda-base process that was considered to be more compatible with spent liquor recovery. Rayonier completed an engineering study for such conversion and even obtained proposals for necessary new equipment, but costs were much higher than anticipated. Therefore, Rayonier decided to stay with its ammonia-base sulfite process.

The mill uses a fully bleached ammonia-base sulfite process from batch digesters. In the digester, cooking acid contains 7–8% total SO_2 as either free SO_2 or ammonium bisulfite. Pressures and temperatures vary with the pulp being produced. The cooked pulp is discharged into blow-pits and transferred to red stock washers where about 90% of the residual red stock liquor is removed from the pulp.

This red liquor contains about 10% of the dissolved solids from the process, and was dispersed in the Strait.

Operational change

Key to the recovery operation is seven spent liquor evaporator bodies that produce the most efficient and rapid concentration of spent pulping liquor solids to a combustible state.

Ecodyne Corporation's Unitech Division (Union, N.J.) designed and built an evaporator system that would concentrate spent red liquor for burning and SO_2 recovery. Vapor recompression pumps were recommended that could economically reduce steam at boiler pressure for other uses in the mill, while at the same time transfer the energy difference to the liquor vapors being pressurized.

Rayonier recovery utilities superintendent Randall Starr explains that up to this point, the turbogenerators and reducing stations satisfied low pressure steam requirements. "With the new system, the compressor turbines act also as reducing stations," he said.

The design was chosen to provide only as much vapor recompression as could be compatible with steam reduction needs. The remainder of the evaporation could then be accomplished in a four-body steam-energized evaporator system.

How it works

The system's design called for an overall evaporation rate of approximately 560 000 lbs/h, with an extra 10% for catch-up or pull-away capacity. The

evaporation capacity of the 3-stage vapor recompression system was 450 000 lbs/h. This portion of the system was not oversized because the flexibility in the vapor recompression is built into the system with variable loadings on the steam turbines. The multiple-effect evaporations operate between approximately 110 000 and 160 000 lbs/h evaporation rate, over a range of 25–52% solids, thus providing the extra 10% catch-up capacity.

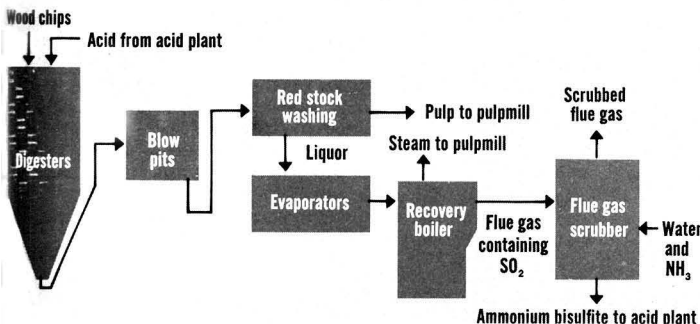
To accommodate the mill's variable low-pressure steam requirements, the vapor compression pre-evaporator section was designed as three completely separate falling-film units. If low-pressure steam requirements are low or if one body is taken off line for wash, the entire system associated with the body, including compressor and turbine drive, is also taken off line.

Compressed vapor is energy source

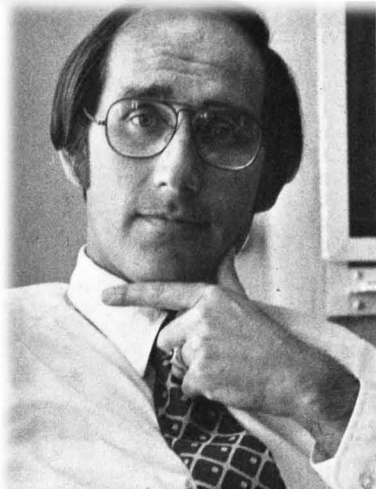
In the 3-stage Vapor Compression Falling-Film (VRFF) system, the heating medium is the vapor removed from the red liquor and increased in both temperature and pressure by a turbine-driven vapor compressor. When the spent liquor enters the VRFF units from the SO_2 stripper, it contains about 10.7% solids. Effluent from the third stage of the VRFF system is 25–30% solids and is ready for the four-body Preheat Falling-Rising-Film (PFR) evaporator system. Vapors from evaporation at 15 psia are compressed to approximately 21.5 psia. The saturation temperature is increased from 213 °F to about 232 °F.

Because the boiling temperatures and liquor viscosities are slightly different in each of the three stages, the actual volume of vapor produced in each stage is correspondingly different. The advantage of turbine compressors is apparent here. As compressor vapor inlet volume decreases to maintain the desired compressor outlet pressure, the turbines slow. Operating the units at reduced capacity is not a problem, and reduced evaporation rates caused by scaling or fouling of the heat transfer interfaces usually do not pose a problem in maintaining nominal pressures and temperatures. If inlet vapor volumes drop too low, the system will shut down automatically.

Cleaning up ammonia base-sulfite processing



OUTLOOK



EPA's Talley submits . . .



Congressmen Teague & Brown request . . .

EPA Office of R&D's five-year projections

"If comprehensive information is available to all interested parties . . . the decision-making process has a chance, at the very least, of surviving the major pitfalls of misinformation and erroneous assumptions."

—A Review of the U.S. EPA
Environmental Research Outlook,
Office of Technology Assessment

In April 1975, Congressman George Brown's Subcommittee on the Environment and the Atmosphere held hearings at which EPA presented its research posture for the next several years. Sensing the tenor of the subcommittee's legislative intent, Wilson Talley, assistant administrator for research and development, ordered the Office of Planning and Review to prepare a comprehensive report outlining EPA's research outlook through fiscal year 1980. This five-year plan was officially and voluntarily transmitted to Congress in February 1976.

Talley's sixth sense was borne out in July 1975 when HR 7108, EPA Research and Development Authorization Bill for Fiscal Year 1976, was introduced by Congressmen Olin Teague (D-Tex.), George Brown (D-Calif.), and Marvin Esch (R-Mich.). This bill would require the EPA to submit annually to Congress a comprehensive five-year program for environmental R&D. HR 7108 passed the House that July and, after a contentious

period, is expected to pass the Senate this legislative session.

In the meantime, in a spirit of cooperation and good politics, the Office of Planning and Review informally delivered a draft of its plan to Brown's subcommittee. This draft eventually found its way to the Congressional Office of Technology Assessment (OTA). But not before December 1975 when Teague, chairman of the Committee on Science and Technology and Brown, chairman of the Subcommittee on the Environment and the Atmosphere, formally asked OTA to review EPA's R&D plan. Brown further requested that his subcommittee be briefed on OTA's findings in February 1976 during its considerations of EPA R&D authorizations for fiscal 1977. By then, Brown also had Talley's final plan in hand.

After Teague's and Brown's request received the approval of OTA's Board of Directors, Robert F. Daly, special assistant to OTA's director Emilio Q. Daddario, began assembling staff and three outside panels whose members, representing many professions, were culled from industry, academe, nonprofit research institutes, public advocacy groups, state agencies, and private consulting firms. In addition to the panels' review of EPA's plan, the OTA staff interviewed key officials in EPA's Office of Research and Development (ORD), and personnel from

other federal agencies conducting environmental research. OTA's work came to an end with the transmittal of its review of ORD's research plan to Congress this past June.

The caveat

OTA's review carefully stresses that this five-year plan is the first of its kind ever prepared by EPA, and the first ever submitted to Congress. It has the defects of most first attempts. But, it was submitted voluntarily and it does offer a refinement to EPA's ongoing dialogue with Congress and an extra dimension to the decision-making process. The plan may even be a harbinger of things to come. Should Congress find this procedure useful it may require long-range planning reports from other federal agencies.

As an agency, the EPA was formed almost six years ago as an amalgam of environmental programs from several federal agencies. The new agency inherited 40 separate and functionally diverse laboratories that it had to integrate into one comprehensive research program to support its regulatory responsibilities. These responsibilities are defined by nine major environmental statutes and several legislative directives tacked onto appropriations bills.

Simply stated, EPA, and especially ORD, is saddled with the responsibility of



and OTA's Daly & staff review . . .

responding to sudden and unanticipated environmental crises—the latest being the Kepone disaster in Hopewell, Va. But, in addition to these firefighting operations, the agency must, as Talley himself has stated, be responsive to longer-range concerns. It is, in fact, this latter area of responsibility that OTA cites as EPA's major shortcoming.

The major deficiency

In its assessment, OTA finds little evidence of EPA's commitment to long-range environmental research—especially environmental management research. Where longer-range goals are spelled out, they are defined in terms of developing techniques rather than issues; but even here the rationale for developing control technology is not discussed.

The plan's ancillary deficiency is, of course, excessive emphasis on immediate or short-term R&D projects to assist in the setting or implementation of standards—efforts that EPA perceives as its primary mandate. Accordingly, EPA's plan stresses the development and demonstration of control technologies to the detriment, according to OTA's assessment, of socioeconomic and exploratory research.

OTA does point out that ORD may be undertaking research to meet its primary responsibility, which is to support the regulatory functions of EPA. This primary role is mandated by sections of major environmental legislation, and was urged upon EPA in an earlier assessment of its R&D program by the National Academy of

Sciences. Since EPA is operating under a shrinking R&D budget, it may very well feel that it has to respond to the well-defined requirements of supporting regulatory needs and by-pass the hazier horizons of long-term exploratory research.

In this regard, OTA recognizes that ORD has thoroughly defined the research needs required to support its immediate regulatory role, though the agency has not

clearly defined how it plans to go about doing this.

When is a plan not a plan

A workable planning document sets objectives and describes strategies and priorities to meet these goals. It also discusses potential constraints in financial and human resources.

The EPA R&D plan, although an impressive compendium of short-term en-

Highlights

EPA says it will...

- Demonstrate fine particulate controls in steel making
- Develop methods for sludge processing; alternative wastewater disinfection techniques
- Identify methods to remove sulfur, nitrogen and trace materials from coal and coal-cleaning wastes

OTA says it should...

- Monitor, characterize and control small particles (<3 μ diam)
- Address conflict of interest issue emanating from role as developer and regulator
- Explore pollution control of new industrial technologies or changes in industrial energy and raw material sources
- Conduct research on the operational, economic and institutional issues of wastewater management

Control and abatement technology

Transport, fate and monitoring

- Characterize and conduct toxicity screening for selected pollutants
- Develop sampling, analysis methods to identify and measure condensable emissions from mobile and stationary sources

- Develop a monitoring screening program to detect toxic substances
- Establish a central monitoring program
- Study processes linking source emissions to their effects on the biosphere
- Design balanced research program on effects of microorganisms and chemical toxicants

- Characterize and identify sources of urban-rural air pollution
- Develop integrated air and water-quality data-base keyed to energy developments

Health and ecological effects

- Evaluate health risks of indoor pollutants
- Identify interactions in health effects of criteria and noncriteria pollutants
- Develop scientific basis for secondary air-quality standards

- Better understand and manage indoor air quality
- Delineate effects of chronic, low-level exposures to pollutants
- Initiate noise research
- Develop a system for predicting the existence of a harmful substance in the environment

Socioeconomic research

- Develop benefits methodologies to assess gains in environmental programs
- Delineate socioeconomic and demographic factors associated with environmental health

- Integrate socioeconomic research into environmental management
- Analyze, develop nontechnological approaches to environmental management
- Analyze competing forces of environmental quality and economic developments

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vironmental research problems, fails as a workable planning document. OTA cites the plan's major defect as a failure to set program priorities and to relate these priorities to general program goals. No where does the plan discuss

- alternative research packages with different mixes of basic, control technology, socioeconomic and health effects research
- the impact of future changes in industrial processes, materials, and new energy sources on the environment
- the function of EPA's 15 field laboratories in the implementation of planned research
- industrial or public input
- a sharing or coordination of environmental research among the various federal agencies, except for the inter-agency energy/environment program
- how it will be used as a planning document within and without the agency.

OTA feels that the deficiencies in the EPA plan stem from an incompletely conceptualized planning process that failed to explore alternative research schemes or resource allocation. This incomplete preparation is even reflected in the structure of the plan. The indefinite way that the research programs are presented makes it impossible to ascertain whether the plan represents a balanced program; it also prevents Congress from monitoring EPA's progress and achievements.

Pollutant-of-the month syndrome

A well thought-out anticipatory research program would add a new dimension to EPA's five-year plan. With the expected changes in social structure, technology and material resources that could significantly affect the environment, such an exploratory program, designed to anticipate problems, would help relieve the agency of its involvement in the fire-fighting episodes that have occurred at an increasingly alarming rate during its short life.

An adequate screening program to detect and identify toxic materials, singly or in combinations in the various media, and the search for early-warning indicator specimens—programs now absent in the agency's plan—would do much to eliminate the "pollutant-of-the-month" syndrome. Proper environmental management implies the need for anticipatory research programs.

Allocation of resources to basic and exploratory research would also aid in the development of control strategies. The OTA review cites NO_x emissions as one example. The chemical form of nitrogen in fossil fuels is not well understood. If it were, a method for its removal prior to the combustion of these fuels could be developed that would at least reduce NO_x emissions.

As it is becoming more evident, total

reserves of these carbonaceous fuels are dwindling. EPA recognizes this and ORD's plan does list energy recovery from domestic wastes, biomass, solar, wind, and geothermal sources. Yet, the plan lists no project to assess the environmental implications of the large-scale use of these energy sources. Future constraints on environmental degradation may call for the increased utilization of these alternate, clean sources of energy. With the long lead times required to get a handle on emerging problems, ORD should begin studies on these energy sources now—so says the OTA review.

Other federal agencies are doing related or apparently duplicative research. The National Cancer Institute for instance has an ongoing screening program for potential carcinogenic substances. The National Institute of Environmental Health Sciences is developing test systems to evaluate potentially toxic materials. NIOSH is developing criteria for recirculating air systems to protect the indoor environment. EPA could tap these sources. Better coordination of federal environmental research programs could relieve EPA of some of the burdens that it is now carrying alone.

The ORD plan reveals a lack of leadership in coordinating or overseeing environmental research within the federal province, according to OTA. Except for its role in coordinating the 12-member inter-agency energy-environment program (see *ES&T*, April 1976, p 324), EPA has shirked its mandate as the lead agency in federal environmental research whose total budget has been estimated at \$1.3 billion (EPA's portion is about \$257 million).

Fixed on the technological fix

The plan clearly reveals EPA's preoccupation with control or treatment methodologies. "Nonstructural/non-treatment" strategies to environmental management have not, according to the OTA review, been sufficiently developed or even analyzed within ORD. Most discouraging is the fact that neither the plan nor the interviews with key personnel unearthed a predilection on EPA's part to remedy this defect.

OTA's review calls for a realignment of priorities from single-purpose abatement strategies to all-encompassing environmental management programs. OTA feels that EPA would benefit from more comprehensive policy analyses that would explore the social, economic and environmental implications of policy decisions as these relate to the costs/benefits of alternative research strategies.

It is OTA's contention that environmental schemes based on the technological fix are increasingly doomed to failure since it is becoming more evident that institutional constraints, not technological restraints, are more problematical and more resistant to resolution. LRE

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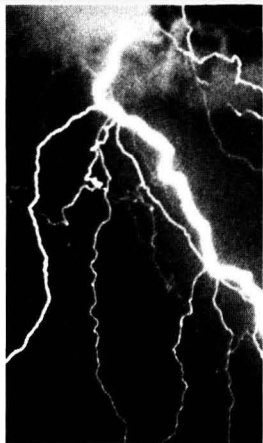
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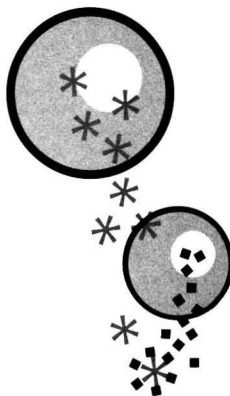
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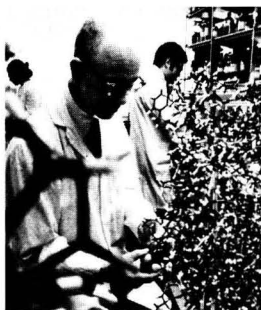
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Progress in smelter emission control

As you approach the Canadian city of Sudbury, Ontario, from the west, along the Lake Superior Route of the Trans-Canada Highway, you pass two unique landmarks. On the left is a numismatic park at which large replicas of coins are on display; on the right is the copper smelter of International Nickel Co., Ltd. (INCO), which has the tallest stack in the world—1250 ft 9 in. The stack's builder was Canadian Kellogg Co., Ltd., a subsidiary of Pullman-Kellogg Co. (Houston, Tex.). In the U.S., the tallest smelter stack is that of Kennecott Copper at Magna, Utah, also built by Pullman-Kellogg. What these tall stacks have in common is high-level dispersion, and significant ground-level reduction of SO_x and other chimney emissions. Opinions as to how well tall stacks do this job at smelters, or power plants, vary widely, to say the least! The EPA, for example, generally endorses neither the use of such stacks nor intermittent controls.

The control picture becomes more involved with the concept of "best available control technology" (BACT) and "significant deterioration" rules as proposed in the Clean Air Act Amendments bill. If this bill becomes law, there could be very tight

requirements concerning copper smelter siting and capacity, as well as separation between smelters. Moreover, these requirements, including 3- and 24-hour increments, could vary with air-quality class. For example, under House Class II increments, copper smelters must be at least 12–18 mi apart, whereas a 9–11-mi separation would be allowable under House Class III increments, by which air could deteriorate to National Air Quality Standards. The bill's Senate version would not allow such deterioration, since it omits Class III.

A U.S. Department of Commerce (DOC) staff study warns that House Class I provisions could preclude non-ferrous smelter sitting in that air-quality zone, even if the smelter has BACT. The study says that in that zone, a smelter might have to be so small as to be impractical, or so far from other smelters as to be uneconomical, particularly if copper smelters, for instance, must be located 15½–20½ mi apart. Also, for example, a 1500 tpd copper smelter would have to be 13–28 mi from a Class I boundary, if it meets source performance standards. Presently, 12 to 13 copper smelters—there are about 20–30 non-ferrous

smelters in the U.S.—would not meet this requirement, according to the DOC study.

Associations

To work toward solutions to air pollution control (apc) problems, the copper smelting industry, in 1971, formed the Smelter Control Research Association, Inc. (SCRA, Columbus, Ohio), and this year, the Smelter Environmental Research Association (SERA, New York, N.Y.). Ivor Campbell of Clyde Williams and Co. (Columbus) is executive director of the SCRA, and Ralph Smith of the University of Michigan is technical director of SERA.

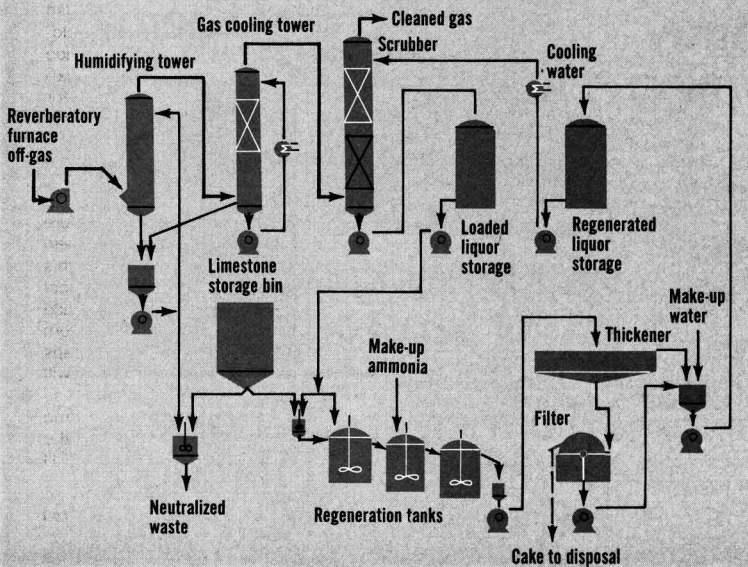
Much has been said about wet-limestone scrubbing of SO₂-laden flue gases. The SCRA added its view to what has already been said very often—essentially, "there has to be a better way," as far as smelter, and particularly copper reverberatory (rever) furnace gases are concerned. Among complaints listed by the SCRA as of 1973 for wet-limestone scrubbing for this application, developed from pilot studies, are that

- The process is not reliable.
 - Downtimes are excessive.
 - There are no reliable criteria for scale-up to commercial models.
 - SO₂ recoveries are not satisfactory.
 - There is a real risk that limestone scrubbing may become obsolete before its problems can be resolved.
- SCRA plans to devote its efforts to other processes that would avoid problems that it sees as inherent in limestone systems, and that would offer promise of greater reliability and SO₂ recovery.

Nevertheless, one must start somewhere, and SCRA certainly did not ignore the limestone option. Indeed, limestone was among the SO₂ reactants first tried for reacting SO₂ from rever furnace tail gas in pilot studies at McGill, Nev.; other reactants studied were hydrated lime, and sodium sulfite with lime regeneration. In 1974, the SCRA and the U.S. Bureau of Mines (BuMines) engaged the C-E Lummus Co. to conduct an engineering evaluation of various soluble scrubbing processes.

More recently, SCRA sponsored a 4000-scfm pilot plant (start-up April 1975), using the ammonia-double-alkali

Ammonia double-alkali process



The industry is upgrading old practices, and introducing new techniques, in order to clear the air

scrubbing process. A feature is limestone regeneration of scrubbing liquor and avoidance of soluble salt production. This plant, at San Manuel, Ariz., removes more than 90% of the SO₂.

Reverb problems

A principal problem with reverb copper smelters is that their gas streams contain as much as 1–2% SO₂. Apparently too much for the wet-limestone scrubbers coming into use at electric power plants, this concentration is also unsuitable for acid plant feedstock. However, a solution must be found if air quality rules are not to sound the death knell for the reverb furnace.

According to a recent report by Carl Rampacek of the University of Alabama, and James Dunham of BuMines, the Bureau's Citrate process is being pilot-tested at a lead smelter. SO₂ is absorbed in a buffered citrate solution and reacted with hydrogen sulfide (H₂S) to produce sulfur. The citrate buffer is regenerated, and two-thirds of the sulfur is reconverted to H₂S for recycling. Remaining sulfur can be stored or sold. Costs are estimated to be 3–4¢/lb of copper, if this system was used in copper smelting, and no credit was taken for the sulfur. More than 2000 h of experience indicate SO₂ removal exceeding 95%.

SO₂ is not the only problem facing smelters. Particulate emissions can contain arsenic, which is toxic. For example, officials of Anaconda Co. (Anaconda, Mont.) themselves have said that the Anaconda smelter emits about 12 tpd of arsenic. Prior to 1971, the company trapped and collected arsenic, also a copper ore by-product, and offered it for sale. ASARCO (New York, N.Y.) stopped buying arsenic that year. However, Anaconda expects that new pollution control equipment, to go on stream later this year, will lower the arsenic emissions to a few lbs/h. This equipment uses a water-quenched gas stream to condense volatiles, and a baghouse to remove particulates. The company will keep the arsenic-laden material collected by the equipment, and see if any commercial use can be found for it.

Getting away from reverb

To comply with present and anticipated

air-quality rules, and, perhaps, to save energy, copper companies are looking at other smelting techniques, including electric furnace smelting, flash furnace smelting, and continuous smelting. Additional approaches involve the Queneau-Schuhmann (Q-S) oxygen process, the AMAX pyrometallurgical process for chalcopyrites, and hydrometallurgy.

The Q-S process uses oxygen in flash melting to smelt copper and nickel sulfide ores in a single reactor from which gases cannot escape. This process produces much of its own heat, and is being used at INCO (Sudbury). Off-gas can have as much as 80% SO₂—enough not only for an acid plant, but for actual SO₂ liquefaction. INCO produces 1 million t/yr of sulfuric acid and 200 000 t/yr of liquid SO₂ from these tail gases, and has an arrangement for handling these by-products through Canada Industries Ltd., in Sudbury. Reputedly, INCO is upgrading its process to a proprietary technique for increasing the SO₂ concentration on an even more economical basis. So is ASARCO (Tacoma, Wash.) and Phelps Dodge (Ajo, Ariz.).

The AMAX (Carteret, N.J.) process now under development would use fluid-bed roasting at 850–900 °C to remove about 97% of the sulfur. The SO₂ concentration in the tail gas would be 12–14%—enough to justify an acid plant. Fugitive emissions would be eliminated. Experience is being gained from a 3.67 tpd pilot plant.

Wetting-down party

Air pollution considerations, as well as a need for processing methods that can be economical on a small scale, have encouraged R&D on hydrometallurgical processes. One such process, the Anaconda Arbiter process, extracts copper from sulfide concentrates by oxygen-ammonia leaching below 100 °C, with residue beneficiated to recover further copper and silver values. Leachate copper is extracted by solvents, and recovered through electrowinning. A prototype plant at Anaconda, Mont., was designed for 36 000 t/yr of electrolytic-grade copper produced by this method.

A commercial plant at the Hecla-El Paso Natural Gas Lakeshore Mine near Casa Grande, Ariz., in "shakedown"

SCRA members

ASARCO

The Anaconda Co.
Cities Service Co.
Copper Range Co.
Inspiration Consolidated Copper Co.
Kennecott Copper Corp.
Newmont Mining Corp.
Phelps Dodge Corp.

SERA members

AMAX

ASARCO

The Anaconda Co.
Bunker Hill
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Inspiration Consolidated Copper Co.
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status earlier this year, will handle fluid-bed roasting of 400 tpd of sulfide flotation concentrate to obtain a sulfate calcine leachable with dilute sulfuric acid. Acid for vat-leaching of copper oxide ores will come from roaster off-gas; the copper itself is to be recovered by cementation.

Cyprus Mines is working on the Cymet ferric chloride process in which chalcopyrite (sulfide ore) is leached; iron and copper values are leached out, and elemental sulfur is produced. Ferric chloride is regenerated during copper electro-winning and electrolytic iron production. A pilot plant near Tucson, Ariz., with a 25-tpd feed produces 7 tpd of copper powder.

Also near Tucson, Duval Corp., a subsidiary of Pennzoil Co., has tested its Clear process for copper and iron leach and ferric chloride regeneration, and is building a 32 500-tpd facility at its Esperanza Mine. The Clear process also makes sulfur. Ferrous and cuprous chloride solutions are electrolyzed to produce copper. Ferrous chloride is further oxidized to regenerate ferric chloride for leach and precipitate excess iron in hydroxide form.

Fast change

In the last half-dozen years, copper ore processing practice in the U.S. has been changing fast. Among reasons for this change are the search for economical ways to recover copper from lower-grade ores, and protection of the public from adverse environmental effects. Perhaps a have-your-cake-and-eat-it situation will evolve, in which supplies of copper—so vital to the world economy since time immemorial—will be assured, while the nation's air and water are kept clean. JJ

Cleaner water for better health

Conferees at the IOI Forum on Ozone Disinfection took a close look at purification efficiency, problems, progress, prospects, and costs

There is no panacea for drinking water and wastewater disinfection and treatment; if there were, it would be in universal use, and conferences on the subject would be quite unnecessary. This lack of panacea generates a need for frequent exchanges of knowledge and views concerning the best approaches to disinfection and treatment. Such an exchange took place at the Forum on Ozone Disinfection held at Chicago, Ill., in early June, and sponsored by the International Ozone Institute, (IOI), now headquartered at Syracuse, N.Y. About 200 water and wastewater technologists from the U.S., Canada, France, Israel, and West Germany met at this forum.

IOI president Morton Klein reminded a forum press conference that more than 1000 operating drinking water plants throughout the world incorporate ozone into their treatment processes. Of these, the great majority are in Europe; however, 21 are in Canada's Province of Québec, and two are in the U.S. Under construction at Montreal is the world's largest ozone plant for drinking water, whose capacity, in U.S. gal, will be 600 mgd (*ES&T*, July 1975, p 618). Klein also told the press conference that for the past six years, considerable R&D and demonstration effort has been exercised to evaluate the use of ozone in place of chlorine for disinfection of sewage plant effluents.

Chlorine substitute?

Ozone in place of chlorine? At first, such a situation may be hard to picture. Indeed, as Alan Hais of the EPA told the forum, projected increases in the use of chlorine between 1974-1983 are 7-15%, at least, and possibly even 4%/yr. He said that perhaps, after 1983, there would be a decline in chlorine use as raw water quality improves, and alternatives are perfected; the emphasis here is on the word "perhaps". For the meantime, it seems to be EPA's view, as expressed by Hais, that cost-effective alternatives to chlorine have not yet been developed for U.S. use.

Nevertheless, Hais made it clear that EPA would not turn its back on alterna-

tives to chlorine. First of all, he pointed out that in the last five years, unit prices for chlorine have trebled. Also, there is risk involved in its transport and handling. Moreover, excessive use of chlorine probably causes damage to aquatic life, and may produce chemicals toxic to humans through combination with other substances, especially man-made or even naturally occurring organic substances in water.

Nevertheless, it is not EPA's business to specify disinfection methods, but to protect public health, as Hais put it. For those who want a clearer picture of the agency's views on disinfection, he recommended a report called, "Disinfection of Wastewater, Task Force Report" (EPA 430/9-75-012). It can be obtained by writing to the General Services Administration, Centralized Mailing List Services, Building 41, Denver Federal Center, Denver, CO 80225, and asking for MCD 21.

Some U.S. ozone use

Whether or not the EPA ever specifies ozone, somebody certainly is doing so, if



IOI president Klein

"now, over 1000 plants use ozone"

one is to judge by some wastewater treatment (wwt) plants now, or soon to be in operation. For example, at Estes Park, Colo., near Fort Collins, there will be a plant of 1.5 mgd with two-stage denitrification, multimedia filtration, and ozone disinfection. The ozonation will be done by two 75-lbs/d Welsbach Ozone Systems (Philadelphia, Pa.) generators. The contactor is of a serpentine-flow, 6 mg/l, diffused-gas configuration.

Ozone disinfection will also be found near Cleveland, Ohio, and should be starting up this month. The ozone will be used at the 4-mgd Meander River plant, using two-stage oxygen-activated sludge—Union Carbide's UNOX wwt system (*ES&T*, October 1975, p 911). The UNOX, ozone generation, contacting, and oxygen recycling are furnished by Union Carbide's Linde Division, Union Carbide's Harvey Rosen, also an IOI member and corporate sponsor, told the forum.

In 1978, look for a 105-mgd wwt plant with 8 mg/l of ozone to start up at Woodlands, Tex. Ozone will be generated from air, and the contactor will be of a packed-bed configuration. However, if you should wish to see a plant that has been in operation since 1974, and has a "track record", take a trip to Indiantown, Fla., to the 600 000-gpd ultrasonic/ozone plant supplied by TII Ecology, Inc. (*ES&T*, July 1975, p 619).

The word from France

French ozone technologists have been consistent in sharing their approximately 75 years of experience in water treatment through the IOI. Much of this experience was garnered by Compagnie Générale des Eaux (CGE, Paris) and its ozone generator-producing arm, Trailigaz. This year, Trailigaz shared much more of its expertise than it ever had before.

The Paris suburban plants at Choisy-le-Roi, Neuilly-sur-Marne, and Mery-sur-Oise treat 800 000, 600 000, and 270 000 m³/d, respectively, with required dosages, during normal operations, of 1.5-2 ppm of ozone generated from dry air in a high-frequency system. Pre-chlorination, flocculation, and rapid filtration compose

Disinfection process cost comparison

| Disinfection process alternative | Technology | Total Process Cost (\$/1000 gal) | | | Capital Investment (\$1000) | | |
|---|------------|----------------------------------|-----------|-----------|-----------------------------|----------|-----------|
| | | Plant size (mgd) | | | Plant size (mgd) | | |
| | | 1 | 10 | 100 | 1 | 10 | 100 |
| Ozone (oxygen) | Existing | 5.91–7.37 | 2.69–4.13 | 1.54–2.68 | 105–147 | 553–851 | 3341–5750 |
| | Advanced | 5.28–6.62 | 2.36–3.49 | 1.20–2.13 | 105–147 | 553–851 | 3341–5750 |
| Ozone (air) | Existing | 5.91–9.15 | 2.99–6.26 | 2.39–4.18 | 147–222 | 865–1430 | 5472–9561 |
| Chlorination | Existing | 4.35–6.96 | 1.23–1.87 | 0.64–1.49 | 52–79 | 159–260 | 627–1126 |
| Chlorination + SO ₂ + dechlorination | Existing | 5.59–9.59 | 1.79–3.54 | 0.88–2.26 | 64–96 | 180–349 | 746–1412 |
| Chlorination + SO ₂ + dechlorination + post-aeration | Existing | 9.02–12.67 | 2.45–4.24 | 1.21–2.59 | 116–148 | 260–429 | 1096–1759 |
| Chlorination + carbon + dechlorination | Existing | 17.62–23.31 | 6.79–8.94 | 4.24–5.23 | 362–389 | 989–1410 | 8627–9126 |

Source: IOI forum paper by Hussein Naimie

the treatment scheme at these plants, François Damez of CGE said.

CGE's Jean Chedal took a look at ozone effects on micropollutants (dissolved organics), especially some that are suspected carcinogens, at initial concentrations of 0.2–100 µg/l. He said that ozonation brings sharp reductions, though not always fully satisfactory, with a 4-min contact time, and 0.4 g/m³ of ozone. While he said that more research on ozonation techniques and degradation compounds is indicated, he did point out that at least two potent carcinogens—3,4-benzopyrene and indenopyrene—are virtually wiped out with this ozone treatment.

For sewage treatment, Cyril Gomella of SETUDE (Paris) gave figures of achievement of 200 coliform bacteria/100 ml (U.S. EPA standard) with unfiltered wastewater, 9–15 ppm of ozone, and 13½ min contact time—generally an E. coli reduction of 10⁻⁵. Color reductions of 60–85% and COD reductions of 45–89%, based on 120 pilot tests, was reported to the forum.

Dollars

In almost any discussion of the relative advantages of different systems, the question of costs will come up, and so it did at the forum. Jack Matson of the University of Houston (Tex.) gave some cost figures comparing chlorine with ozone; he also noted that in some areas, such as Houston, sodium hypochlorite (NaOCl), rather than straight chlorine, may be used, because hazards in shipping and handling of chlorine have led the city of Houston to ban the use of gaseous chlorine.

For a 100-mgd municipal wwt plant, Matson pegged capital costs (6.25% interest) at \$4.8 million, with operation and maintenance (O&M) at \$108 000/yr with chlorine, or \$238 000/yr with NaOCl. With ozone, capital costs on the same terms might be as high as \$10.7 million, with

O&M costs at \$191 000/yr if ozone is made from air, or \$87 000/yr, if ozone is made from oxygen. On the basis of unit costs/1000 gal, Matson concluded that ozone at 5 ppm can be competitive if it is generated from oxygen, and used on a once-through basis. Plant life is assumed to be 20 years.

Since the supplier of a chlorine or ozone system will be an industrial firm, the presentation of cost estimates by such a firm would be of great interest to a conference such as the IOI forum. These estimates were offered by Hussein Naimie of the Eimco BSP Division of Envirotech Corp. (Salt Lake City, Utah).

Biocidal effects

Ozone seemed to achieve a 97.3% poliovirus inactivation with a contact time 2.8 mg/l-min after 4 min, although even 0.9 mg/l-min worked well, V. Riesser of the University of Louisville (Ky.) School of Medicine, told the forum. But how was this accomplished? One possibility may be severe virus capsid damage, as shown by effects that Riesser said only ozone could have brought about on these capsids, which were labeled with carbon-14. The capsid, or lipid protein casing of the virus, consists of four polypeptides of molecular weight 7000–32 000, approximately, and it is these that showed heavy disruption after exposure to ozone. Riesser advocated further research to see whether the virus RNA is still infectious after ozone treatment.

Los Angeles County is evaluating a 72 000-gpd ozone pilot plant for wwt. The object is to determine cost-effectiveness of ozone to achieve fecal coliform kills to 200/100 ml or less (EPA standard for discharge to navigable waters), and to 2.2/100 ml or less total coliforms (California standard for unrestricted recreational reuse). Henry Ghan of the country's sanitation district advised that for most effective ozonation to achieve a good

coliform kill, COD should not exceed 12 mg/l; suspended solids, 5 mg/l; nitrite, 0.1 mg/l; or color, 10 units. Higher contaminant levels, Ghan warned, could blunt the desired biocidal effects of the ozone.

Old/new approaches

Ozone can be used with ultraviolet (UV) light to remove chlorinated hydrocarbons, including PCB's, H. W. Prengle of Houston Research, Inc. (Tex.) explained to the forum. He reported better than 99% removal. Also, William Ward of Olin Water Services (Kansas City, Kan.) said that chlorine dioxide (ClO₂), used since the late 1930's at the Niagara River, for example, but becoming more "popular" now, is an excellent selective oxidant, microbicide, and viricide. He pointed out that ClO₂, at 2 ppm, also removes metals such as iron and manganese, and can break up cyanides, phenols, and other organics without leaving noxious chlorinated organic residues. In the U.S., for instance, ClO₂ is used to destroy phenols that would otherwise go into the Niagara River, and to kill fouling algae at Philadelphia, Pa. Full-scale ClO₂ generating equipment, made by Olin, is small—42 by 42 by 14 in., Ward said.

Thus, there are alternatives for water treatment and disinfection of which ozone is but one. Indeed, it might not always be the desired alternative; for example, for seawater-cooled cooling towers, chlorine presently seems to be as effective, or more effective as a biocide, John Garey of Marine Research, Inc., said. However, for many applications—acquaculture, hospital wwt, municipal and industrial wwt, and drinking water treatment, including disinfection, to name a few—ozone seems to be coming into increasing use. In numerous cases, ozone systems still need study and "debugging", but it can be expected that ozone will eventually play a very prominent role as a water cleaner and disinfectant. JJ

Testing air filter efficiency

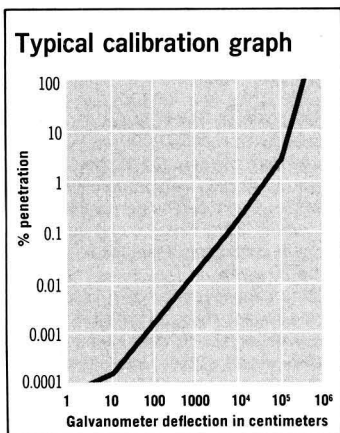
The sodium flame penetrometer satisfies certification requirements in England and compares favorably with other test methods, but Balston Ltd. warns that it cannot predict long-term liquid aerosol retention efficiency

Ever wonder how air pollution control experts decide exactly what size and how many very small particles pass through high-performance air filters? This question is frequently asked of manufacturers of filters that are used to remove sub-micron size particles from air streams, since there are a wide variety of test methods used in the filtration industry.

R. M. Farrow, managing director of Balston Ltd. (Maidstone, England) says, "the company is often asked how it determines the filtration efficiency of its high efficiency Filter Tubes." Balston filters are used advantageously as protective devices on sensitive and expensive monitoring instruments (*ES&T*, September 1974, p 790). Farrow says that the choice between the myriad methods depends on two main factors:

- nature, size, and concentration of the contaminant particle
- sensitivity, reliability, and the ease of use of the penetration-detection system.

"There are really very few standard methods for high efficiency filter rating", Farrow says. "The primary tests are SFP (sodium flame penetrometer), DOP (dioctyl phthalate), and methylene blue test. There are also a number of rather cum-



bersome tests based on gravimetric determinations using standard test dusts (fly ash, aloxite and Arizona road dust). Some of these have the status of standards but are difficult to set up under controlled conditions."

The English affiliate of Balston, Inc., chose the sodium flame penetrometer (SFP) as the standard test for its product. This test method has the advantage of

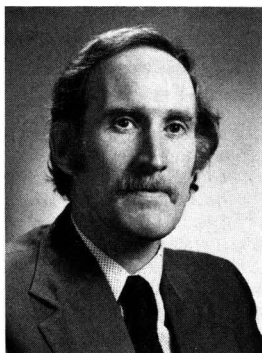
being a recognized standard test in Great Britain. Balston's sodium flame penetrometer has been certified to British Standard BS4400 by the United Kingdom Ministry of Defence, Chemical Defence Establishment, which is the Certification Authority in the U.K.

How it works

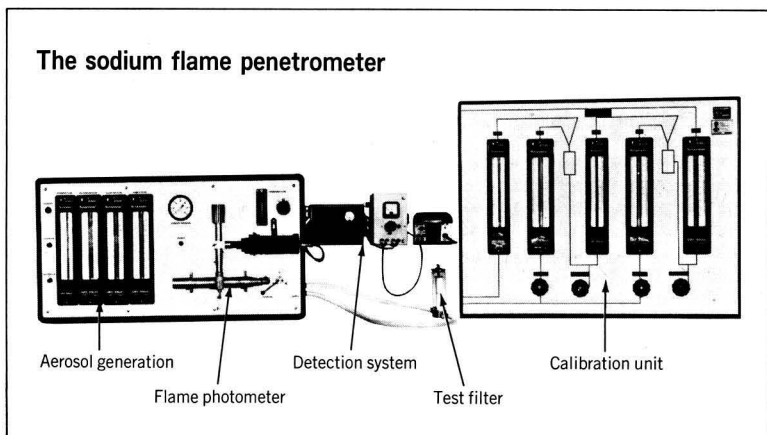
The particulate test cloud is a standard aerosol of sodium chloride particles of 0.6 micron mass median diameter (diameter range 0.01–2 microns) generated by the atomization of a 1% solution of aqueous sodium chloride under standard conditions. The aerosol is diluted with air and presented to the filter at a standard face velocity of 10 cm/s.

A fixed proportion of the cloud penetrating the filter is vaporized in a hydrogen flame that is viewed by a photomultiplier through suitable light filters; the resulting photo current is measured by a galvanometer. The galvanometer deflection is linearly proportional to the mass of salt passing through the flame, up to a concentration of 8% of the unfiltered cloud, after which the deflection increases more slowly than concentration.

The instrument is calibrated by successively bleeding off and diluting to dif-



Balston's Farrow
"few methods for filter rating"



ferent degrees the cloud and salt particles. A calibration graph of percentage penetration against galvanometer deflection can be constructed.

Other test methods

For many years, the test method most widely used in the U.S. for high-efficiency filters has been the di-octyl phthalate (DOP) test. This test uses a nominally mono-disperse aerosol of 0.3-micron diameter generated by the evaporation and subsequent condensation of DOP, with assessment of concentration by light-scattering methods.

Farrow says, "the ratio of efficiencies of a filter tested using both SFP and DOP aerosols varied considerably with the type of filter and more specifically with face velocity. At moderate face velocities (12 cm/s) the SFP efficiency is generally equal with the DOP efficiency. At lower face velocities, the SFP gives a lower value than the DOP test, while at higher face velocities, the SFP records higher filter efficiency values than the DOP test".

Caution

It must be remembered that both the SFP and DOP tests measure only the initial retention efficiency of the filter. Neither test can be used to predict the performance of filters for removing liquid aerosols from air or gas streams over a long period. Balston rates its coalescing filter elements (Grade BX) by using oil aerosols over an extended period of time. Filter grades giving the highest retention measured by the SFP do not necessarily give best coalescing performance.

The most difficult particles to filter are those of 0.1–1.0 micron diameter. These are respirable particles and include bacteria. It is generally accepted that a SFP rating of more than 99.997% qualifies a filter for most gas sterilization applications. Tests have shown that fibrous filters with a SFP retention of more than 99.999% will pass less than one organism in 10^8 (airborne bacteria at approximately 1 micron diameter).

The efficiency figures for Balston grades A and AA filter tubes (>99.9999%) are higher than the level normally accepted for sterilizing filters by a factor of at least 10. It is also important to note that under most conditions these filters will remove the much smaller viruses about as well as they remove bacteria.

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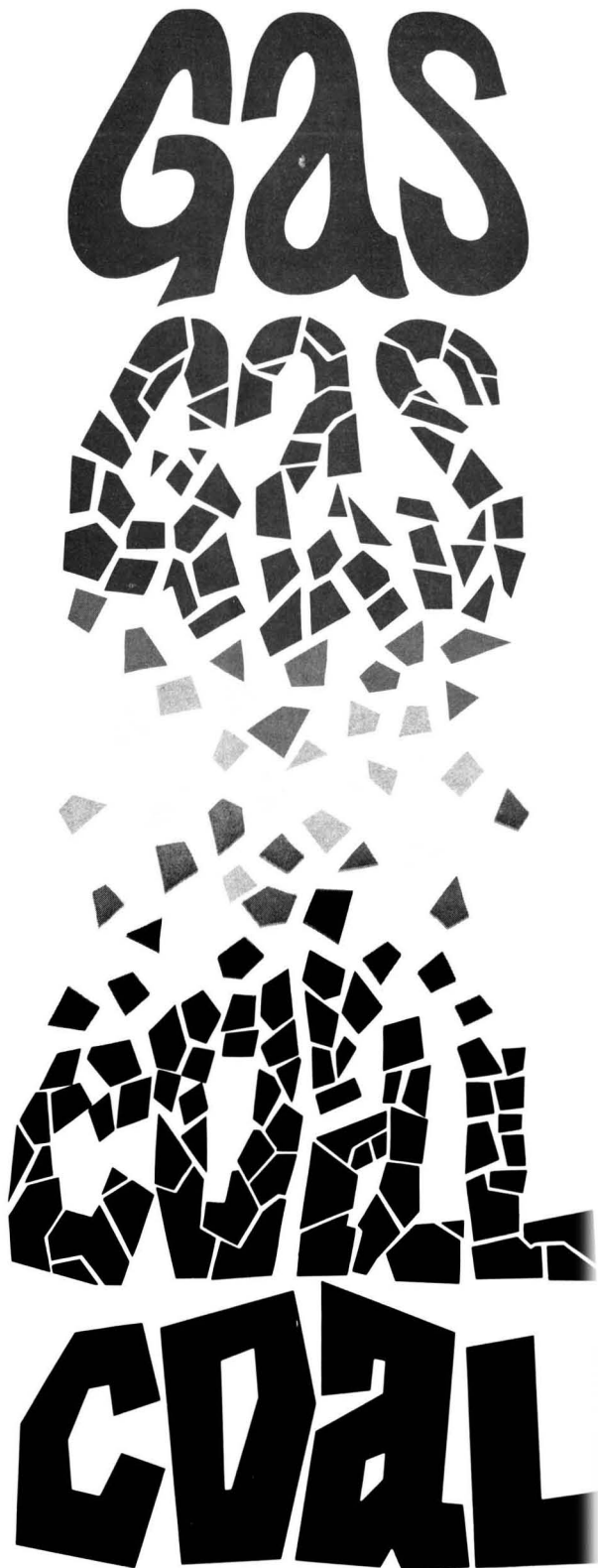
FEATURE

ERDA's fossil energy activities

Synfuels from coal and enhanced methods to recover oil, natural gas and oil shale may be competitive and socially acceptable options to alternative energy sources in the not-too-distant future

Philip C. White

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Highlights of the direction of ERDA's activities

The Energy Research and Development Administration (ERDA), established January 19, 1975, inherited the coal, petroleum, natural gas, and oil shale programs that principally originated in the Department of the Interior's Office of Coal Research and the Bureau of Mines. The newly created agency greatly expanded its horizons for fossil energy technology in 1975-76. During this year it moved toward the implementation of large demonstration projects for converting coal to clean fuels.

Significant progress also was achieved in developing the Fossil Energy Research Program. Here ERDA was able to enlist university participation and to secure industrial contributions to cost-sharing projects for the enhanced recovery of petroleum and natural gas.

The new Fossil Energy organization, headed by an assistant administrator and a deputy assistant administrator, consists of five program divisions:

- coal conversion and utilization
- fossil energy research
- fossil demonstration plants
- MHD (magnetohydrodynamics)
- oil, gas and shale technology.

Staff offices include Program Planning and Analysis, an Administrative Office, and the Senior Staff for special assistance and counsel.

The conversion and utilization of coal, the Nation's most abundant fossil fuel, was given high priority in ERDA's National Energy Plan. An updated version of the Plan, issued in April 1976, placed more emphasis on conservation. Light-water-nuclear reactors and the enhanced recovery of oil and gas were also ranked as fuel sources that could be tapped to bridge the energy gap between now and the year 2000. After these energy sources, ERDA foresees the successful development of more inexhaustible supplies of energy such as the breeder reactor, solar, electric, and fusion.

Fossil energy activities

In essence, the Fossil Energy program seeks to develop and demonstrate, in conjunction with industry, the technology necessary for establishing a synthetic fuels-from-coal industry, as well as for improving methods to recover petroleum, natural gas, and oil shale. These objectives have the potential for being economically competitive with alternate energy sources and environmentally and socially acceptable in the near-term (by 1985) and mid-term (by 2000).

To achieve its objectives, the Fossil Energy program has grown substantially, as reflected by the dramatic increases in budgetary funds. In fiscal year 1975, expenditures totaled \$204 million, nearly triple the \$76 million expended in fiscal 1974. In fiscal 1976, the budget increased to just under \$350 million and, for fiscal 1977, funding requests amount to \$442 million (Table 1). These figures do not reflect cost-sharing funds put up by contractors.

Industry cost sharing is concentrated in the more advanced phases of coal conversion and in the enhanced recovery of oil and gas, although there is some agency cofunding in earlier developmental stages. A typical development sequence from

- A request to industry and others for technical proposals to design, construct and operate a demonstration plant for converting coal to pipeline-quality (high Btu) gas. ERDA received five proposals that were being evaluated. Such a plant would supply data for scale-up to commercial-sized facilities producing gas from coal and/or lignite.

- A request for proposals (RFP) to design, construct and operate demonstration projects for converting coal into clean fuel (low Btu) gas for power generation and on large- and small-scale industrial users. Fourteen firms responded to the RFP.

- Award of contracts to develop engineering information on magnetohydrodynamics (MHD) generators and systems for testing in a component development and integration facility to be built near Butte, Mont.

- RFP's to perform studies of high-temperature gas-turbine-combined cycle development program operating on coal or coal-derived fuels. Four large manufacturers were selected to perform the first phase of a six-year program at the initial cost of approximately \$9 million.

- Selection of the Curtiss-Wright Co. (Wood-Ridge, N.J.) to negotiate a contract to build and operate a pilot electric generating plant using advanced technology to burn high-sulfur coal. The plant would use a coal-fired, pressurized fluidized-bed combustion technique to power steam and gas turbines in a combined cycle operation.

- Initiation of site preparation work for the H-Coal pilot plant to be built at Catelettsburg, Ky. The plant, the largest of its kind, would process up to 600 tons of coal daily in the production of clean liquids.

- Issuance of a program opportunity notice (PON) for proposals to develop and demonstrate a fluidized-bed concept for clean burning of high-sulfur coal and coal waste in industrial boilers and heaters. Thirteen proposals were received from industry and cost-sharing contracts are expected to be awarded by the end of 1976.

- RFP's to design, develop, test and evaluate valves to be compatible with operating conditions encountered in various coal gasification plants.

- Issuance of two RFP's to demonstrate methods for recovering oil from tar sands.

- Issuance of two RFP's for field demonstration projects with use of a micellar-polymer chemical flooding process to recover crude oil. One of the RFP's asks for small pilot projects, the other for one large-scale project, using the recovery technique.

- RFP's for projects to stimulate natural gas production by hydraulic and chemical explosive fracturing methods that could release the vast amounts of fuel now locked in tight geological formations.

- RFP's for field demonstration projects with use of carbon dioxide injection methods to recover crude oil from shallow underground reservoirs.

- RFP's for field demonstration projects with use of thermal processes to recover crude oil.

- The award of millions of dollars in cost-sharing contracts with industry to test improved methods for the enhanced (secondary and tertiary) recovery of oil and gas. By 1985, ERDA expects this technology to add 2 billion barrels of oil and 10 trillion cubic feet of natural gas to U.S. reserves. This would mean an increase in production of 500 000 barrels of oil per day and 3 billion cubic feet of natural gas per day.

- Distribution of a PON seeking proposals for the development of technology to recover shale oil in place.

- Launching of a new program to stimulate the production of natural gas from Devonian shale in the eastern U.S. Trillions of cubic feet of gas, locked in tight formations, cannot be developed economically with current technology.

Table 1. ERDA's 1977 request to Congress for fossil energy programs

| Coal | \$ million |
|--|------------|
| Coal liquefaction | 73.9 |
| High-Btu gasification | 45.0 |
| Low-Btu gasification | 33.0 |
| Advanced power systems | 22.5 |
| Advanced research and supporting technology | 37.0 |
| Direct combustion | 52.4 |
| Demonstration plants | 53.0 |
| Magnetohydrodynamics | 37.4 |
| Total coal program | 354.2 |
| Petroleum & natural gas | 36.9 |
| In-situ (oil from shale and coal gasification) | 30.6 |
| Total operating expenses | \$422.0 |

concept to pilot and demonstration projects requires from 15–20 years, but overlapping sequences can reduce this time to a degree. This sequence of scaling up engineering data to demonstration projects will provide information for cost estimates and design of commercial plants.

To date, ERDA has defined several demonstration projects for translating advanced concepts into commercial use, with one—a clean boiler fuel plant—already underway. The others include a pipeline quality gas plant aimed at residential and commercial heating, and a fuel gas plant for electric power utilities or industrial uses.

In conjunction with this essential scaling up of second-generation technologies, President Ford has proposed a Synthetic Fuels Commercialization Program directed at constructing a limited number of plants in the 1980's. By using present day processes to produce synthetic fuels for the marketplace, these plants could yield valuable economic, environmental, regulatory, and institutional data needed for commercializing both first- and second-generation technologies.

The transfer of pilot-plant technology to the demonstration stage gained impetus in January 1975, with the award of a \$237 million contract to the Coalcon Co. (New York, N.Y.). The firm proposes to design, build and operate a coal-to-clean-boiler-fuels demonstration plant on a site near New Athens, Ill. For other highlights, all laying the foundation for technical advances on a larger scale, see box material.

The Fossil Energy research program expanded steadily in 1975–76, particularly in the area of university support and materials research. At the academic level, the annual rate of expenditures increased from \$2.9 million in fiscal 1974 to \$8.6 million in fiscal 1975 and \$14 million in fiscal 1976. The number of projects increased from 48 in fiscal 1975 to about 80 in 1976.

Second-generation technology

The coal conversion and utilization effort is directed toward demonstrating second-generation technology on a near-commercial scale in the early 1980's. A variety of processes is being

developed to convert eastern and western coal to liquids and gases. Although some processes may appear to be similar, technical differences in key aspects of the processes make them suited for a particular rank of coal, type of product, or plant site.

Coal conversion processes are being developed to convert this fossil fuel into products that substitute for those derived from oil and natural gas. These substitutes will include: crude oil, fuel oil, and distillates; chemical feedstock; pipeline quality (high Btu) and fuel (low and intermediate Btu) gas; and other by-products such as char that may be useful in energy production. The liquefaction, high Btu, and low Btu sub-programs are designed to develop these products and their use in the market.

Coal utilization programs are developing processes that would permit increased use of coal by direct combustion in utility, industrial/institutional boilers, and process heaters, as well as primary fuel for electric power generation. These objectives may be attained through improved direct combustion systems, advanced power systems with gas turbines, and MHD electric power.

Liquefaction. Products derived from coal liquefaction compete in two distinct markets. One market uses low-ash, low-sulfur boiler fuels suitable for clean electric power generation and industrial steam generation; the other uses high-grade fuels such as gasoline, methanol, diesel oil, heating oil, and chemical feedstocks.

Several problem areas have been identified; for example, solid/liquid separation and utilization of remaining solids for the generation of hydrogen. As part of the solution, the revamped Cresap, W. Va., Test Center will permit pilot testing of advanced solid/liquid separation concepts, and the evaluation of valves, pumps, and other auxiliary equipment. The information collected will be fed into the pilot-plant program (such as the Solvent Refined Coal plant at Tacoma, Wash.) and into current and future demonstration projects.

High-Btu gasification. Improved gasification processes should produce a substitute natural gas (SNG) with a heating value of approximately 950 Btu/ft³ with combustion characteristics similar to natural gas but essentially free of sulfur and other pollutants.

The processes are distinctive in that each represents a different approach to the technique of high-Btu gas production. The first-generation Lurgi gasification process that incorporates a methanation step is being used as a guide to determine if any of the processes under development are, in fact, improvements over existing technology. Improvements are measured primarily in terms of comparative capital and operating costs, and the ability to operate successfully with American caking coals.

Four gasification processes are relatively advanced in their development. The HYGAS and CO₂-Acceptor pilot plants are currently operating. The Synthane pilot plant is being readied for operation, and construction is completed on the Bi-Gas pilot plant. A fifth plant, steam-iron, produces hydrogen from char for use in other coal gasification or liquefaction processes. A sixth project, a process development unit (PDU) that uses the self-agglomerating ash process, is nearing completion. The program also includes the pilot-plant study of alternate techniques for methanating intermediate-Btu synthetic gas, including a new concept called liquid-phase-methanation.

Low-Btu gasification. The three most likely markets for low-Btu gas are electric power generation, industrial heating, and chemical feedstocks.

The major milestones for low-Btu projects are the operation of an atmospheric, entrained-bed PDU; operation of a two-stage pressurized, fluidized-bed gasifier PDU with sulfur removal by



Coal gasification. The Bi-Gas pilot plant recently completed at Homer City, Pa.

limestone; the design of a combined cycle pilot plant with a pressurized, entrained bed; and the operation of a molten salt PDU.

In addition to the conventional above-ground gasification projects, underground or in-situ gasification processes are being developed by ERDA. The in-situ method potentially offers economic and environmental benefits over conventional mining and gasification. In such processes, coal deposits are chemically reacted in the ground and low- to intermediate-Btu gas is extracted in a manner similar to that used with natural gas.

The major effort to date consists of field tests at Hanna, Wyo., a technology based on vertical wells for generating a low-Btu gas to be used for power generation. Another approach to in-situ gasification involves evaluating directional wells drilled in thin eastern coal seams. A third project, using the packed-bed process, is planned to gasify thick western coal seams to produce an intermediate-Btu gas; this gas may be upgraded to a synthetic high-Btu gas by surface processing. Pilot projects for these last two approaches are being planned.

Advanced power systems. These systems are directed toward the use of coal-derived fuels in an environmentally acceptable manner at lower cost than current electric power generating systems. Specifically, developmental efforts are directed toward improved gas turbines for combined cycle systems and topping cycles in order to use high combustion temperatures more effectively. The two major categories of advanced power systems—open and closed cycle—are undergoing comparative studies.

Energy Conversion Alternative Studies (ECAS) are being undertaken to determine which systems would be economically

attractive, which could be ready for commercialization before 1985, which appear decidedly uneconomic, and which require further study to determine their economic potential.

Specific closed-cycle projects are in the process of being started. Open-cycle systems will be developed to a technology readiness stage before proceeding to full-scale prototype development. Technical problems center around the effects of high temperatures and pressures. Materials, corrosion, erosion, and gas cleanup will be subjected to extensive study in the experimental facilities to be built.

Direct combustion. The objective is to develop and demonstrate on a commercial scale the direct combustion of high-sulfur coals without exceeding pollution standards. Fluidized-bed combustors containing sulfur oxide sorbents will be used in the burning of coal.

The program focuses on both atmospheric and pressurized, fluidized-bed boiler technology for powerplant and industrial/institutional heat uses. Initial efforts are concentrated on atmospheric systems having broad applications in both electric power generation and industrial heat and steam. Also, pressurized combustion is being examined to evaluate its full potential.

Direct combustion technology has near-term (1985) potential as an economic and efficient coal-fired alternative to existing boiler systems that use scrubbers for emissions control. Equipment based on this technology is expected to find a market both in new equipment installations and in the replacement of process heaters and boilers fired by natural gas. The latter applications are desirable because of continuing shortages in natural gas.

Fossil energy research projects

- Systems studies to determine the optimum coal and shale conversion systems for further development and eventual commercial use. These studies point the way to synfuel commercialization in both the near- and mid-term future.
- Materials and components problems encountered in pilot demonstration and commercial plants of present and second-generation conversion processes.
- Direct utilization relating to corresponding projects in coal conversion and utilization and relatively near-term in nature.
- Processes work with a longer-term schedule; advanced conversion processes to be commercialized primarily after 1985.
- University projects particularly suited for academic analysis.

Fossil energy R&D

As the central research and systems studies area for all elements of fossil energy, the Fossil Energy Research Division conducts projects in the ERDA Energy Research Centers, National Laboratories, other government agencies, private industry, and universities. See box material for projects undertaken by this Division.

The general objective is to demonstrate on a near-commercial scale the more promising processes developed and evaluated in industry and government R&D programs. The fossil demonstration plant program provides the final step toward coal and shale utilization as future clean energy sources; it is partially funded through engineering, construction, and operation of processes on the verge of commercialization.

The first phase of each demonstration plant project (conceptual commercial plant process and mechanical design) will be funded entirely by ERDA. The second phase (detailed engineering, procurement and construction) and the third phase (operation) will be funded on a cost sharing 50/50 basis by the government and contractor.

As noted earlier, several demonstration plant projects have been defined. This program includes coal conversion to synthetic liquid fuels that range from heavy fuel oil to distillates; conversion to pipeline quality and fuel gas; and direct combustion of coal and integration of power production.

Magnetohydrodynamics (MHD)

An MHD electrical generation system utilizes a topping cycle combined with a bottoming conventional steam plant to achieve greater plant efficiencies. Essentially, MHD systems, both open and closed cycles, convert coal to a conducting hot gas that moves at high velocity through a magnetic field to produce power.

Basic feasibility of the open-cycle system has been established; it has been demonstrated that an MHD generator can operate by utilizing the products of direct coal combustion. However, engineering data for design and construction of pilot-scale facilities are not yet available.

The open-cycle program is structured to progress through three overlapping phases, the first focusing on specific development requirements leading to the design and construction of an engineering test facility (ETF). The second phase carries the ETF into an advanced engineering stage; the third phase covers possible design, construction, and operation of a commercial-scale plant.

Exploratory work also has been performed on closed-cycle systems; work has concentrated on heat exchangers and generator problems. Closed-cycle systems development is not as advanced as open-cycle systems. Current work is addressed to basic physical issues.

MHD research is aimed at demonstration of performance and prolonged operation of channels; development of components and integration of key subsystems; and integrated operation of MHD systems with electric utilities.

Petroleum, natural gas, oil shale

Petroleum and natural gas will continue to be the Nation's main fossil energy resources in the years ahead. ERDA's efforts are directed toward increasing the production of oil and gas by advanced production and recovery techniques and toward improving the efficiency of petroleum use and re-use.

Oil extraction efforts will demonstrate existing and improved secondary and tertiary recovery techniques rather than new refinery technology. Industry already has a broad technological base in refining.

The natural gas program is designed to stimulate the commercial production of natural gas from tight geologic formations containing vast quantities of fuel. These domestic reservoirs have remained untapped because they cannot be developed economically with current technology. Now being tested are advanced methods that include massive hydraulic fracturing, combinations of hydraulic and chemical explosive fracturing, and fracturing wells deviating from normal to intersect with natural fractures.

Fluid injection and fracturing methods for gas and oil extraction will be used in field demonstration projects. Solvent recovery methods for heavy oil and in-situ combustion methods for tar sands will be developed and demonstrated.

The goals of the oil shale program are: reducing the water requirements of the oil shale industry through in-situ processing; increasing the recoverable reserve base through improved production technology; and ensuring that environmental safeguards are built into the in-situ oil shale process. Advancing in-situ production of shale oil to commercial feasibility is targeted for the early 1980's.

The oil shale program emphasizes in-situ retorting rather than surfacing retorting, which is considered a proven technology. In addition, laboratory and bench-scale studies on composition and conversion of clean fuels from oil shale have been initiated to provide a technology base for improvements and new process development.

Summation

As the foregoing summary suggests, careful planning and long-term commitment by both the government and industry are essential to the attainment of energy self-sufficiency. Continued cooperation and accelerated scientific achievement will hasten that end and thus preserve a high quality of living and reinforce the goals of national security.



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Coordinated by LRE

How the Army does a bang-up job of treating effluents

Is it possible to combat water pollution at ammunition plants, and save money and resources? Yes, it is, and here are some ways that this is done

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Most of the Army Ammunition Plants (AAPs) that exist today were built during the early 1940s; their sole mission was to manufacture and supply ammunition for U.S. armed forces engaged in a world war. After the war, manufacturing ceased; some of the plants were "moth-balled", and some remained on a "stand-by" status. Most were reactivated during the Korean and Vietnam conflicts. Presently, of the 27 AAPs, about half are still active, but in these, production is significantly limited.

Army Ammunition Plants are essentially huge self-sufficient manufacturing complexes occupying 5000–30 000 acres. Most generate their own electricity and steam, and have their own wells and water treatment plants. They normally landfill or incinerate their own refuse and treat their own sewage. AAPs manufacture projectiles, and propellants and explosives (P&E), and load the latter into the former. The production capability for P&E is in the hundreds of tons/day/plant.

AAPs also manufacture many of the starting materials needed to manufacture the P&E; for example, sulfuric acid, nitric acid, acetic anhydride, and ammonium nitrate, as well as reconcentrate and recover spent acids. Some even recover, concentrate, and sell by-products to the private sector. In addition, AAPs buy ton quantities of ammonia, cellulose, toluene, sodium carbonate, sulfur, cyclohexamine, potassium nitrate, charcoal, glycerine, plastic binders, plasticizers, and stabilizers from U.S. private industry.

Although these large industrial facilities are owned by the government, they are operated by private contractors such as Hercules, Olin, ICI United States, Du Pont, Mason, Hanger-Silas Mason, Day Zimmerman, and Uniroyal. Thus, the personnel force at a typical plant may consist of about 50 government and 2000–3000 non-government employees. They are for this rea-

son also called GOCO—government owned, contractor operated, plants.

The pollution abatement drive

The concept of treating industrial wastes produced from the manufacture of ammunition is not new. Efforts to implement pollution abatement technology have been expended over the years. However, with the advent of environmental awareness and of a major munition plant modernization program beginning in 1968, an intensive effort to eliminate pollution from AAPs was initiated. Added impetus to the effort was gained through the publication of Executive Order 11507 in February 1970, later superseded by E. O. 11752, of December 17, 1973. Through these Orders and related documents, the U.S. government, assuming a role of leadership in pollution abatement, directed all federal facilities to set an example for the private sector.

Munitions facilities share a common requirement with private industry to comply with the provisions of the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500), which directs this country toward a national goal that "the discharge of pollutants into navigable waters shall be eliminated." The well-known chronology for achievement of effluent limitations established by this Act requires the application of pollution control technology characterized as "best practical control technology currently available" (BPCTCA) by 1977, and "best available technology economically achievable" (BATEA) by 1983. The goal of "overall zero [pollution] discharge" by 1985 is also clearly an important and demanding objective for industrial pollution abatement efforts. Although most discharge standards specific to AAP manufacturing processes have not as yet been promulgated, the plants are obliged to conform to discharge guidelines imposed by the regional Environmental Protection Agency (EPA) offices and the states wherein they are located. The government abatement efforts therefore are geared to meet specific and well-defined pollutant discharge limits set by the same agencies that set those for the private sector.

The AAP modernization program is under the Army Materiel Command, Project Manager's Office for Munitions Production Base Modernization. In support, Picatinny Arsenal is responsible for the development of pollution abatement technology to permit timely compliance with forthcoming effluent standards. Although emphasis for this technology development project is placed upon pollution problems unique to the munitions industry, much of the technology developed is directly applicable to problems en-

countered by private industry in the manufacture of such products as acids, dyes, pharmaceuticals, and paper. The extensive Picatinny Arsenal program of pollution abatement at GOCO plants has been described (*ES&T*, July 1973, p 806). It is broad-based; addresses solid waste, water and air pollution; and includes participation by Frankford (Philadelphia, Pa.) and Edgewood (Edgewood, Md.) Arsenals, with Picatinny Arsenal as the lead facility. This "omnibus" program, titled "Development of Methods to Minimize Environmental Contamination", was initiated in 1969 and planned for ten years at a cost of about \$30 million.

The three facilities are each assigned certain responsibilities. Picatinny Arsenal has the responsibility of abating pollution at propellant and explosive manufacturing plants and load, assembly and pack (L/A/P) plants. Frankford Arsenal has a similar responsibility for plants manufacturing metal parts. In addition to providing support, Edgewood Arsenal assumes responsibility for facilities manufacturing chemical agents such as those used for smoke-screening operations.

Currently, the Picatinny Arsenal effort incorporates about 20 project tasks, each addressed to a specific AAP pollution problem. The importance of water management (WM) as a tool for water pollution abatement at GOCO plants dictated its establishment as a separate task addressed to all AAP manufacturing processes as well as L/A/P operations. Industrial water management, as part of this program, has proven a vital tool for water pollution minimization. Not only is it a most cost-effective approach, but in light of the zero pollution discharge requirement, it is judged the most viable route to achievement of this 1985 goal. In addition, and most important in view of the current fuel oil situation and the national drive for energy conservation, implementation of WM methodology often results in lower process energy requirements. Thus, the net result is efficient pollution abatement, plus dollars and energy saved for the government, or, synonymously, the taxpayer.

Water management concept

The key concept in industrial water management is the consideration of total plant water utilization avoiding the traditional reliance upon treatment-for-discharge for standards achievement. The latter route is the classical approach to water pollution abatement, whereby physical, chemical, or biological systems are used to remove or detoxify pollutants in plant outfalls (outside the processing section of the plant). For municipal wastewaters, this approach is presently the only acceptable one. For industrial wastewaters, however, such constraints on allowable technology do not exist; thus, a complete spectrum of control and treatment technologies can be applied. The end result is a concept for solving water pollution problems that is less costly, more able to exploit advances in control and treatment technology more fully, and much more amenable to changing effluent standards.

Water management is preventive pollution control that utilizes the basic principles of cooling and process water recycle and reuse with concurrent recovery of contaminants to limit the volume of wastewater discharged. By its very nature, the water management approach does not address mixed waste streams, but deals with aqueous influent, flow, and discharge within the process itself. But while it initially addresses each source of wastewater within each process, it subsequently integrates all processes within an AAP in order to achieve both intraprocess recycle and interprocess reuse.

The cost-effectiveness of such an approach becomes immediately apparent when one considers that AAPs utilize from about 1.5 million to over 300 million gpd of water. All process water is treated prior to use. All process wastewater must be treated prior to discharge (a very costly operation). Recovery of waste chemicals means that less need be manufactured. In addition, and of growing significance, are reduced energy demands, for it requires a good deal of energy to pump and treat water and to manufacture chemicals.

FIGURE 1

NC process

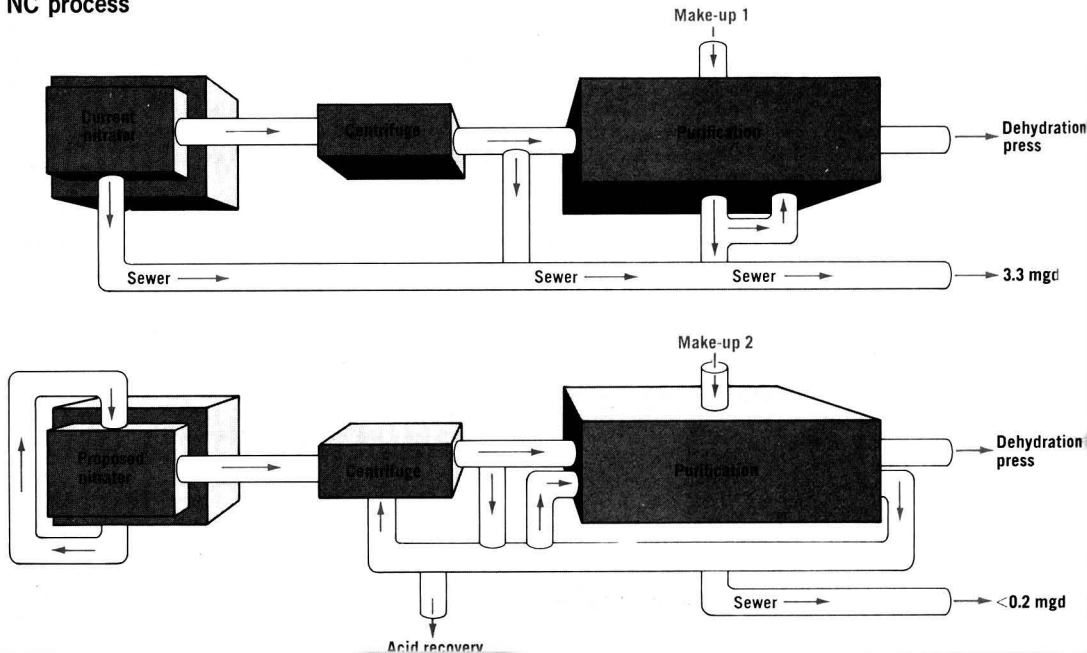
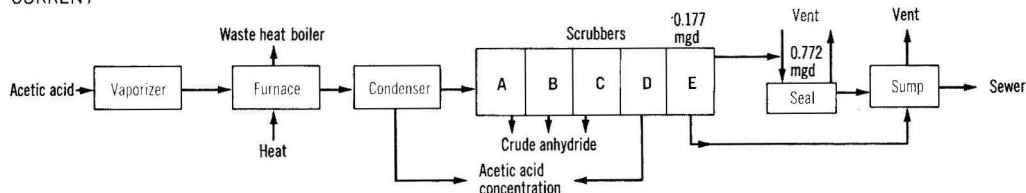


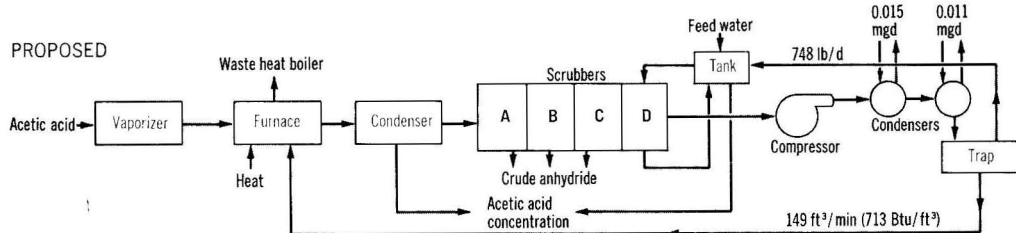
FIGURE 2

Acetic anhydride manufacture

CURRENT



PROPOSED



Water management methodology

The development of an industrial water management program must recognize that abatement of plant-scale water pollution is a complex problem, best resolved by using a structured, comprehensive strategy of mixed technologies. This strategy would include equipment modification, improved product recovery, recycle of acceptable wastewater for repeat operation, recycle of effluent to concentrate contaminants to permit their economical recovery, and wastewater treatment to effect waste chemical recovery and to permit intra- and interprocess water recycle.

Changes in the chemistry or stoichiometry of the manufacturing process, to include the purification and product finishing steps, are not considered within the scope of the WM program at Picatinny Arsenal. This matter is addressed under separate projects dealing with advanced process technology, while WM considerations are generally limited, for example, to towers and conduits, flanges, valves, pumps, and related items that permit recycle/reuse. Replacement of one process unit for another—for instance, a barometric with a surface condenser, or a scrubber with a pump, is permitted, but only for the purpose of reducing water usage or recovering a contaminant for reuse. The propellant or explosive preparation methodology remains unchanged. Indeed, a prime prerequisite to acceptance of a water management measure is assurance that the integrity (physical, chemical, ballistic properties) of the product that is being manufactured is not affected. This assurance is necessary, since all military propellants and explosives must meet very stringent specifications for optimum performance.

The water management methodology applied to date generates information in a stepwise fashion. The steps are identified as

- process water balance and water quality and quantity inventory
- evaluation of data and recycle-reuse recommendations based on discharge limitations, practicability, economics and energy considerations
- prototype evaluation of recommended measures. The application of this methodology has resulted in efficient water pollution abatement accompanied by reduced manufacturing costs.

Water management in NC manufacture

In the continuous manufacture of nitrocellulose (NC), cotton linters or wood pulp are continuously nitrated at a rate of 100–150 lb/min and dumped into a centrifuge. The centrifuge

is operated to remove acid from the NC, and the acid is recovered. The nitrated product is then washed by a spray system and centrifuged again to remove the spent acid. The NC, now containing 58% total acids, by weight, is discharged to a slurry tub where water is added. The NC-water slurry is agitated and then pumped to a boiling tub house as a 10% slurry with an acid strength of 1–1.5%. Additional water is then added to the NC in the boiling tub so that the mixture attains a total acidity level of 0.25–0.50%.

The NC purification steps consist first of acid and neutral boils in tubs to hydrolyze lower nitrate and sulfate esters. Next, beaters cut and pulp the fibers to the desired degree of fineness; pulping also releases residual acid. Alkaline and neutral boils in poachers complete the removal of acid. Removal of foreign solids, blending, and wringing to achieve desired quality and water content complete the purification steps. Water for boils, displacement wash water, and slurry water are discharged to the boiling tub pits for the acid and neutral boils and to the poacher pits for the remaining operations.

Simplified schematics of both the current continuous NC system, as described above, and the visualized system incorporating WM recommendations are depicted in Figure 1. In the current process, over 2 million gal of process water containing about 32 000 lb of nitric acid, mostly, are discharged daily. This necessitates neutralization followed by nitrate removal prior to discharge. In addition, NC fines that collect in the boiling tub and poacher pits must be periodically removed and destroyed (reaction with aqueous sodium hydroxide (NaOH) has proven satisfactory). About 1 million gal of cooling water per day are also used on a once-through basis.

The in-plant control scheme for the continuous NC manufacturing line was devised by the technical staff of Hercules, Inc., contractor at Radford AAP (Radford, Va.) under direction of Picatinny Arsenal. Features of this WM scheme are

- counter-current recycle of neutral waters to control buildup of sodium salts from acid neutralization
- recycle of recovered water for neutral boil, and blender, poacher and beater operations
- recycle of the acidic flume line recycle waters back to a belt filter and centrifuge as the influent stream in the counter-current wash of incoming NC until the waters are concentrated to approximately 60% total acidity
- removal of NC fines via centrifuging, permitting recovery and reuse of fines and continuous recycle of recovered water.

Prerequisite studies in the development of this scheme in-

cluded ascertaining that NC quality was not affected by increasing acid content of acidic flume line and centrifuge recycle waters, as well as successfully demonstrating centrifuging for NC fines removal. Benefits attendant with this scheme include

- elimination of a neutralization/biodenitrification plant
- reduction of process water usage by almost 2 million gallons per day
- recovery of 6.2 t of nitric acid and 1.8 t of sulfuric acid/line/d per day
- virtual elimination of water pollution.

Water management in acetic anhydride manufacture

In this process, used at Holston AAP (Kingsport, Tenn.), glacial acetic acid is vaporized and fed into a cracking furnace heated with producer gas, where it is converted to ketene. After condensing water and unreacted acid are removed, the ketene is absorbed in glacial acetic acid, in a series of three scrubbers, to yield acetic anhydride. The remaining vapor is then scrubbed with 12% cold, aqueous acetic acid. Finally, vapor leaving the weak-acid scrubber enters a water scrubber to remove most of the remaining ketene and acetic acid, thereby minimizing corrosion in the steam ejectors and barometric condensers providing vacuum service.

The water from the last scrubber goes to a drain sump, and from there to an industrial waste sewer. This discharge operation accounts for a loss of about 850 lb/day of acetic acid. The vapor leaving the "water scrubber" goes to a barometric condenser. Non-condensables, consisting principally of methane, ethylene, and carbon oxides, with a calorific value of over 700 Btu/ft³, vent to the atmosphere at a rate of about 150 ft³/minute. Condensate enters the barometric seal and overflows to the drain sump and sewer.

The schematics of both the current system, as described above, and of the proposed configuration resulting from WM studies, are displayed in Figure 2. Proposed equipment modifications are expected to achieve product recovery and detoxification by eliminating both contaminated effluents and vented organics.

Essentially, the elimination of "water scrubber E", steam ejectors, barometric condensers, barometric seals, and drain sump is envisioned. Instead, a centrifugal compressor, which would now be utilized for vacuum service, would take the gas

TABLE 1

Benefits from proposed changes in a 1 million-lb/d acetic anhydride plant

| | |
|--------------------------------------|--|
| Water pollution | Eliminated |
| Air pollution | Virtually eliminated |
| Recovery, reuse of contaminants | 765 lbs/d HAC ^a (\$12 000/yr) 163 ft ³ /min gases (\$78 000/yr) |
| Reduction, process water | 0.92 mgd (\$59 000/yr) |
| Reduction, steam | 257 000 lbs/d (\$39 000/yr) |
| Reduction, post-abatement | > \$1 million |
| Reduction, post-abatement operations | \$102 500/yr |
| Modification implementation cost | \$50 000-185 000 |
| Modification operating cost | \$8204/yr, compared to \$98 560/yr for current |

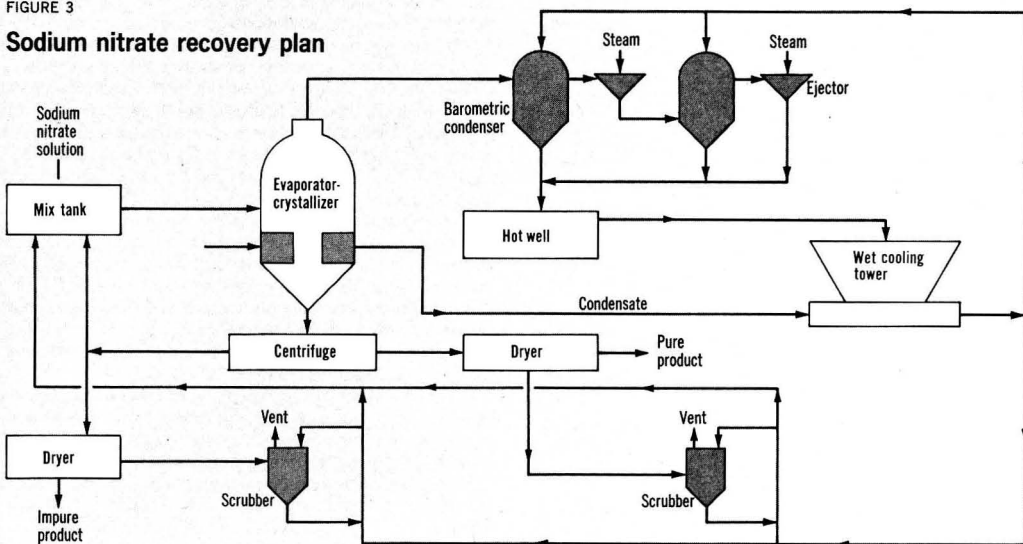
^a HAC = Acetic acid

and vapor mixture from the "weak-acid-D" scrubber and compress it to slightly greater than atmospheric pressure (36 in. of mercury). The compressed mixture would be cooled to a maximum temperature of 38 °F by passing it through two heat exchangers, one cooled with water to 70–75 °F, and the second with refrigerated ethylene glycol to 28 °F. In the heat exchangers, 88.5% of the acetic acid and 88.5% of the water vapor are expected to condense. The remaining gases, at a pressure of approximately 32 in. of mercury, would then be sent to the cracking furnace as supplemental fuel.

Implementation of these proposed water management recommendations is expected to eliminate water pollution, essentially eliminate air pollution, reduce water, steam, and cracking-furnace fuel consumption, and permit the recovery of about 750 lb/day of acetic acid. The quantitative benefits to be derived from the proposed modifications are illustrated in Table 1 together with the estimated costs of implementation. These costs, however, may be recovered at least tenfold, through reductions in end-of-process treatment requirements.

FIGURE 3

Sodium nitrate recovery plan



Water management in sodium nitrate recovery

Holston AAP is unique among munitions plants in not recovering nitric acid remaining after nitration. Instead, the weak, contaminated acid is neutralized with NaOH, yielding sodium nitrate (NaNO_3) plus lesser amounts of sodium formate and sodium acetate. The latter mixture is recovered and sold as agricultural fertilizer. Recovery consists of evaporation-crystallization, centrifuging to yield a "pure" product stream (wet solids), and an "impure" produce stream (mother liquor), and drying in either a fluid bed or rotary dryer. Scrubbers remove entrained product in the dryer off-gases.

The facility is designed to discharge a 1.5-mgd effluent containing 30–40 lb/day of NaNO_3 . The proposed WM schemes for this process are displayed in Figure 3. Effluent from the barometric condensers and steam ejectors, contaminated with product, is recycled after heat removal through a cooling tower. Take-off from the cooling tower sump is fed forward as make-up liquor for the scrubbers, removing product accumulating in the recycle. Condensate from the evaporation-crystallization step finds use as cooling water make-up. Cascading the cooling tower and scrubber increases product concentrations sufficiently that recovery can be achieved by direct return-to-process. The result is total containment of effluents at the process level. Costs to implement this scheme should not be in excess of \$300 000 (early 1974 dollars). In turn, the elimination of this effluent from the collective treatment plant to be built at Holston reduces the construction cost of this facility more than \$1 million.

Water management in TNT manufacture

In the manufacture of trinitrotoluene (TNT) at Radford AAP, nitration is done in a continuous counter-current process involving six nitration stages. The product TNT then flows to the acid washer, a five-stage mixer settler unit, where water is used to remove entrained and dissolved acid. The TNT is fed into the first stage of the washer, and hot water (80 °C) goes into the last stage for counter-current flow. The water from the acid wash, containing about 15% acid, returns to the second nitrator. The TNT goes from the acid washer through two Sellite washers where it is reacted with Sellite solution (aqueous sodium sulfite) to remove impurities and undesirable isomers of TNT. The spent

Red water is an aqueous solution of dinitrotoluene sodium sulfonate salts and sodium sulfite, sulfate, nitrite, and nitrate, which is currently sold to the paper industry as make-up sulfate cake, or incinerated.

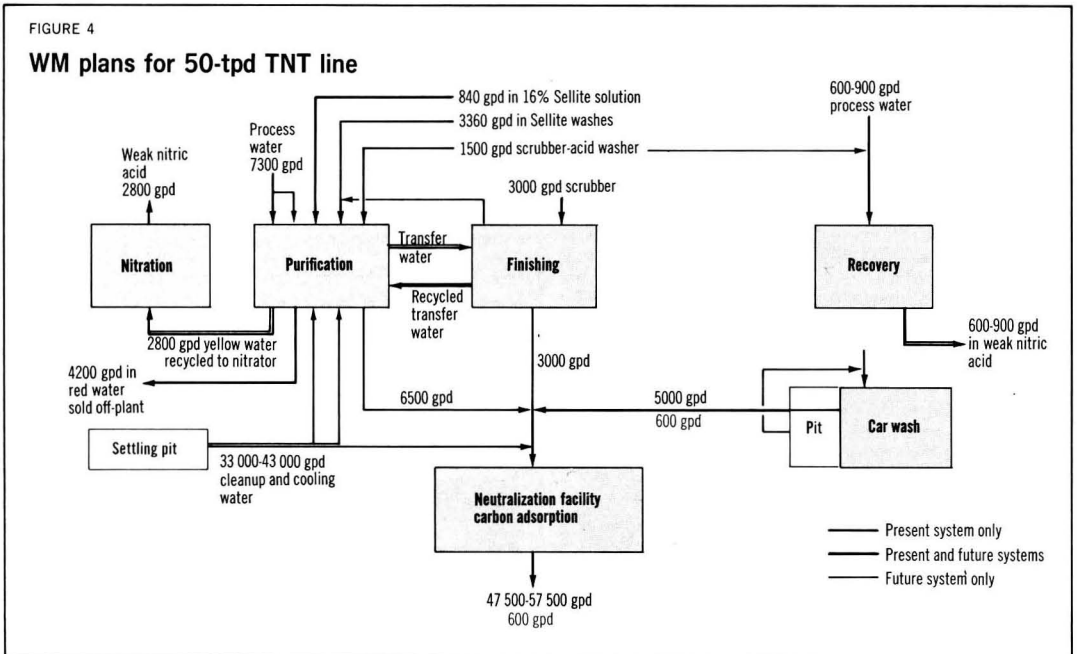
Sellite solution from the first Sellite washer leaves the process as "red water". The TNT from the second Selliting unit goes to the post-Sellite washer where it receives five water washes to remove residual water-soluble impurities.

The water for these washes comes from a water tank in the transfer system. After the post-Sellite wash, the TNT passes to a tank where it is mixed with about three times its weight of water and pumped to a head tank from which it flows by gravity to the Finishing Area. In the Finishing Area, the water and TNT are separated and the water is returned to the Purification Area. Fresh water is added in the transfer system to replace water used in the post-Sellite wash and water retained in the TNT before drying (approximately 10% by weight). Two small, internal scrubber systems are operated on each line in the area, one in the Purification Area with 30 gal/ton of TNT, and one in the Finishing Area with 60 gal/ton of TNT.

The total wastewater discharge to be treated ranges 47 500–57 500 gpd/50 tpd line. The originally proposed and approved abatement facility for the TNT Area at Radford AAP was to include neutralization for the acids, and carbon adsorption for dissolved nitrobenzenes.

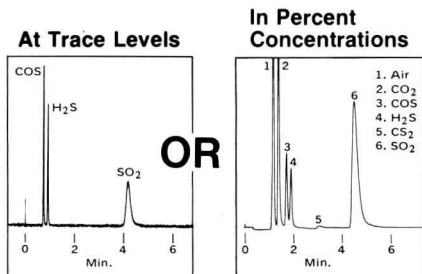
A simplified schematic, plus water balance of one TNT line is shown with solid lines in Figure 4. Excluded from the water balance is 5 million gallons of cooling water, which will be recycled through a cooling tower to be constructed. The dashed lines, also in Figure 4, indicate proposed WM modifications, and include:

- eliminating the scrubber in the acid wash area (the fume recovery system now used to abate NO_x pollution from the ni-



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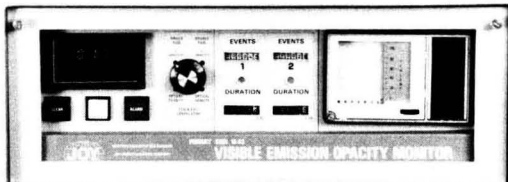


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The car wash area is where the wash-down of tank cars which deliver acids to the TNT area, and spillage from transfer operations take place.

tration building can in addition accommodate the effluent from this area—nitric acid is recovered as a result of this operation.

- returning scrubber water from the finishing area to the purification area for Sellite washes
- recycling water in the car wash area
- recycling general clean-up water to Sellite wash and acid washes
- reduction of process water
- changes in clean-up procedure, such as substitution of vacuum cleaning for water wash-down operations.

The proposed modifications will reduce the wastewater discharge from about 52 000 to about 600 gpd/line. This small volume of water is expected to be of a purity that would permit storage with subsequent reuse or discharge without treatment.

Thus, with the water recycle/reuse system, all water from the TNT Area would be stored and reused in the processes. There would no longer be a requirement for a wastewater treatment facility. For this reason, a recommendation was made to cancel construction of the latter and, instead, to install necessary pumps, pits, and piping to effect the WM modifications. This recommendation was approved by higher command and the Corps of Engineers. Implementation will result in capital cost savings of over \$1 million, and operating cost savings of about \$500 000/yr.

Recovery pays

Industrial water management methodology based on recycling, reuse, and recovery can provide the most efficient and cost-effective schemes for abating pollution at AAPs. Cost benefits can be derived from reduced water usage, reclamation of waste chemicals, smaller post-abatement facilities or avoidance of the need for abatement facilities, and, often, curtailed energy demands.

A number of WM schemes, such as recycling of wastewater in TNT manufacture, recycling of neutral and acidic waters in NC manufacture, and use of centrifugal compressors for vacuum service and vapor recovery, have been accepted, or are under serious consideration. Cost savings to date have amounted to more than \$10 million.



Arrigo Carotti is a project leader in the Modernization and Special Technology Division of Picatinny Arsenal. He is responsible for projects and technology development and assessment for water management applicable to munitions manufacturing processes.



John C. Thomas is chief of the Wastes Treatment Section at Edgewood Arsenal. He is involved in the development of water management programs for Army munitions plants, under the direction of Picatinny Arsenal, and is a registered professional engineer in Ohio.

Coordinated by JJ

National environmental policy: coordination or confusion?

Created to anticipate environmental consequences of human activity, the CEQ uses the environmental impact statement as its primary tool—some say incorrectly and at the expense of its primary mandate

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In recent months there has been considerable controversy involving the role and effectiveness of the Council on Environmental Quality (CEQ). This controversy emanates from the divergent opinions of the role that CEQ has assumed to ensure adequate protection of the environment and the concomitant costs to operate CEQ programs; and the role its critics see mandated for the CEQ under PL 91-190. To gain a proper perspective of the functioning of the CEQ, it is useful to compare and contrast the intended coordinative role of the CEQ as a governing board with its actual activities since its formation.

CEQ's creation

The passage of PL 91-190, the National Environmental Policy Act of 1969 (NEPA), was a direct result of the growing public awareness and concern for the magnitude of environmental pollution. The NEPA was enacted to establish a single national policy for the protection of the environment and to create a governing body to administer the Act.

The expressed purposes of the NEPA are to:

- encourage a productive and enjoyable harmony between man and his environment
- promote efforts that will prevent or eliminate damage to the environment and biosphere
- enrich the understanding of the ecological systems and natural resources important to the nation
- establish a council on environmental quality.

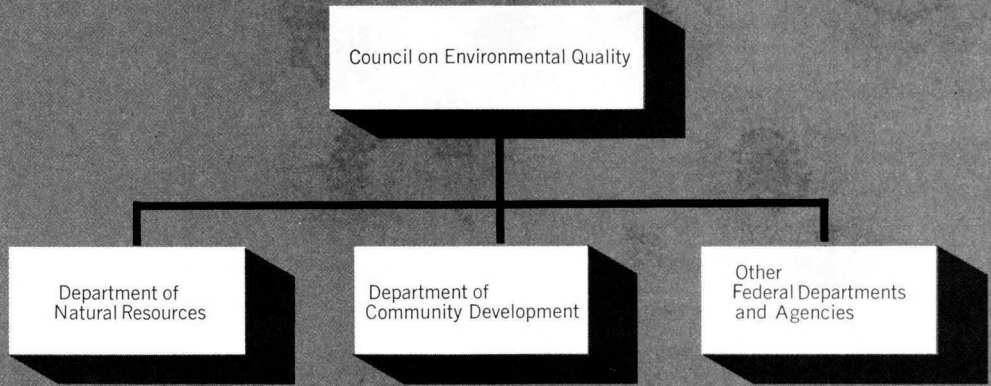
Public Law 91-190 not only created the CEQ, but also spelled out its primary responsibilities as a governing board. This Act, however, does not specifically prohibit anyone from doing anything, but instead requires that there be public consideration or assessment of estimated environmental consequences before actions that would "significantly" affect the human environment are initiated.

The Environmental Impact Statement (EIS) is the principal coordinative mechanism of the CEQ. The EIS, a detailed statement on the effects of proposed actions on the environment, is currently required for all major projects that affect the environment and involve federal support in whole or part through contracts, grants, subsidies, loans, or other forms of funding assistance; and/or a federal lease, permit, license, certification or other entitlement. These impact statements are officially prepared by the concerned federal agency, such as the Corps of Engineers, HEW, and HUD, under the auspices of the CEQ.

Thus, the major thrust of the NEPA is oriented toward federal government-related actions. Private industries are not specifically required to prepare impact statements unless the proposed action requires a federal license or permit, and even in this event the federal lead agency (the federal agency primarily concerned) will prepare the final EIS. However, the applicant (the firm or

FIGURE 1

CEQ's organization for environmental management



Source: *Management Science*, June 1973, p. 1144.

agency requesting action) is usually required to prepare an environmental report, an Environmental Impact Assessments, that defines and analyzes the real and potential environmental impacts of the proposed action.

The CEQ's mandated primary role is to supervise the enforcement of the NEPA functions and to coordinate a single environmental policy, not to make detailed evaluations of each EIS. This function is left to the Environmental Protection Agency (EPA), other interested federal and state agencies, and the public.

In an effort to clearly define the coordinative and administrative responsibilities of the CEQ and to more fully describe the requirements of the other concerned federal agencies, former President Nixon issued Executive Order 11514 on March 5, 1970. The order established eleven governing responsibilities for the CEQ (see box).

The charge to the CEQ as clarified by the Executive Order is clear: The CEQ exists to govern national environmental policy and oversee federal agency actions that affect the human environment. The coordinative relationship of the CEQ to other agencies and departments is represented in Figure 1.

The EIS process

In general if a federally related action or project is determined to have a significant effect on the environment, the lead agency prepares a draft EIS. Supporting documentation for this draft may be prepared by a private enterprise requesting approval for a proposed action. The draft EIS is then forwarded to the CEQ and to all federal, state and local agencies interested in environmental issues for a preliminary evaluation. In addition, this document is made available for public analysis and comment. Comments and testimony received from the interested parties regarding the draft statement are the basis for the lead agency's preparation of a final EIS that recommends a proposed action

be undertaken as originally conceived, modified or abandoned. The completed EIS is then submitted to the CEQ for final review. Although the CEQ has no real legal power to stop proposed actions, it can recommend to the President that an executive order halting the project be issued. At this point, however, pollution control takes on a political coloration and enforcement efforts of the CEQ can be debilitated in a single stroke.

The present EIS process is generally effective in initiating some analysis of the impact of federally associated actions. There are two elements in the process, however, which add considerable confusion and cost. The first such factor concerns the uniformity of impact statements. In accordance with Executive Order 11514, the CEQ has issued general guidelines for the preparation of EIS's that assure some degree of uniformity in final impact statements. These guidelines notwithstanding, various federal agencies have published additional comprehensive guides for the evaluation of environmental parameters that are particular to agency orientation. Confusion results when these agencies have differing EIS guidelines. For example, actions involving energy supply and natural resource development may require review by as many as 85 different federal agencies, each of which may have different guidelines.

The reasoning underlying the issuance of these supplemental guides lies in the NEPA requirement that EIS's make a *specific* determination of the magnitude of the impact and a *detailed weighing* of the significance of an action. However, the complexity and diversity of agency guidelines are often a source of much of the confusion associated with EIS preparation and, to some extent, negate coordinative efforts of the CEQ in promulgating a single national environmental policy.

The second major source of confusion is the inconsistency in the determination of what is a *significant* environmental impact and thus what actions require the preparation of an EIS. Again there are several sets of guidelines identifying what is a significant environmental impact—those issued by the CEQ and those

issued by the various federal agencies. Still, in the confusion of applying these varied guidelines, final decisions on what is significant are often rather subjective and subject to political influence.

Inadequacies of the CEQ

Evidence concerning the effectiveness of the CEQ as a coordinating, governing board is, at this early date, inconclusive and controversial. There are many who support the NEPA and the efforts of the CEQ as the first significant step toward controlling pollution and protecting the environment. At the same time, however, critics point out that the bureaucratic apparatus of the CEQ is ineffective and costly. A sound case can be made to support either camp.

Criticism leveled at the CEQ can generally be categorized under two main charges: That the CEQ has been grossly inadequate in its efforts to curb pollution and promote environmental quality enhancement, and that while the CEQ has made some significant strides, bureaucratic stumbling blocks, red tape, and the costs of EIS preparation have given the CEQ a political emphasis.

Since NEPA was enacted in 1969, the CEQ has reviewed more than 5000 Environmental Impact Statements. Of the 1974 total, about 300 concerned highway projects, 125 watershed projects, 100 energy projects, 75 air transportation projects and the rest miscellaneous projects. The Corps of Engineers reported in 1973 that impact assessments had compelled it to drop 24 projects, suspend 44 others, and significantly modify 197. These seemingly impressive figures are tempered somewhat when it is noted that approximately 75% of all impact statements filed have been the result of highway department and Corps of Engineers actions. Therefore, environmental assessments are highly concentrated in a few, though admittedly important, areas.

Part of CEQ's ineffectiveness may be directly related to the fact that the necessary data, technology and expertise for proper assessment of the impact of actions on the environment are

simply not available. Stephen D. Kelley supports this view in his statement that appeared in *Public Works*:

"The majority of impact statements written to date are too superficial. They lack the comprehensiveness and depth needed for a full understanding of environmental relationships and the impacts resulting from a proposed action. As an example, an analysis of socio-economic impacts requires reference to a regional, long-range development plan which often does not exist."

Certainly, the present inadequacy of technical competence cannot be denied, but can for the most part be discounted as a valid criticism of the CEQ environmental assessment mechanism. It is through the need for new methods of analysis that necessary techniques are developed and the EIS process can be regarded as an important catalyst in that development.

Another major concern regarding the ineffectiveness of the CEQ is in the area of the validity of impact statements; criticisms are most often cited in two areas. First, impact statements are too frequently prepared at the end of the planning process just to satisfy the legal requirements of the NEPA rather than concurrently when they could actually influence design and implementation. Second, in many cases negative information has been purposely eliminated or deemphasized to enhance the environmental desirability of the proposed action.

This latter criticism of CEQ efforts is also rather weak in that there will always be those who will attempt to circumvent the law for their own gain. The courts, however, have generally upheld the spirit of the law as demonstrated by the following court interpretation of the NEPA (*Scenic Hudson Preservation Conference v Federal Power Commission*).

"Congress gave the Federal Power Commission . . . a specific planning responsibility . . . This commission, of its own motion, should always seek to insure that a full and adequate record is presented to it . . . This role does not permit it to act as an umpire blandly calling balls and strikes for adversaries appearing before it; the right of the public must receive active and affirmative protection at the hands of the commission . . . The commission must see to it that the record is complete. The commission has an affirmative duty to inquire into and consider all relevant facts . . ."

In addition to the above criticisms, a study by Frank Kreith, professor at the University of Colorado, gives little support to the effectiveness of the CEQ and the EIS mechanism. His research revealed that out of a random sample of 200 EIS's, none had caused projects to be abandoned because of adverse impacts, although most listed unavoidable adverse environmental effects. For 127 actions for which adverse effects were included, a total of 214 alternatives were listed and all were rejected, 130 for economic rather than environmental reasons.

CEQ's bureaucratic structure

The other major criticism of NEPA and the CEQ is the costly and cumbersome bureaucracy that has been created and fostered. Critics suggest that the NEPA, instead of establishing a governing body to administer a single national environmental policy, has instead produced typical governmental confusion and a plethora of bureaucratic red tape. There is such support for this line of reasoning, and as Michael J. Walker pointed out in an article in *Management Review* (Jan. 1974, p 26), "This (NEPA) has meant a mountain of new paper work and run up costs for everyone, managers in both industry and government complain." Many of these costs stem from the EIS process and the supplemental guidelines promulgated by the various agencies. Moreover, most agree that the final EIS statements are too long and overly complicated and may add one to two years to the already long period between the time a project is initiated and construction finally started. As Robert P. Stearns and David E. Ross pointed out in an article in *Public Works* (Nov. 1973, p 63), "Unfortunately in practice, the EIS requirements have been of-

CEQ's responsibilities spelled out

- Evaluate existing and proposed policies and activities of agencies with regard to pollution control and environmental quality enhancement.
- Make recommendations to the President and agency heads for priority assignments for pollution abatement and environmental quality enhancement programs.
- Identify environmental problems for which adequate policy statements do not exist.
- Conduct public hearings and/or conferences on issues of environmental significance.
- Provide monitoring services for: (a) trends in the state of the environment; (b) environmental effects of public and private action; (c) effectiveness of programs for protecting and enhancing the state of the environment.
- Coordinate federal programs related to environmental quality.
- Solicit international cooperation in environmental quality.
- Issue guidelines to agencies for the preparation of EIS.
- Provide supplementary instructions to agencies as requested.
- Aid the President in the preparation of an annual Environmental Quality Report required by Section 201 of the Act.
- Initiate research and analysis.

TABLE 1.
EPA's track record
in reviewing EIS's

| EPA region | June 1-June 20, 1972 Number reviewed | Number with overdue comments |
|--------------|---|---------------------------------|
| HQ | 8 | 7 |
| I | 7 | 4 |
| II | 2 | 1 |
| III | 21 | 8 |
| IV | 25 | 0 |
| V | 26 | 21 |
| VI | 17 | 9 |
| VII | 15 | 4 |
| VIII | 6 | 4 |
| IX | 7 | 6 |
| X | 8 | 5 |
| TOTAL | 142 | 69 |

Source: Hearings Before the House Committee on Appropriations, 93d Congress, First Session, p 512.

tentimes treated as a mere formality; another red-tape condition that must be satisfied prior to the project initiation."

An example of a project that has been delayed occurred in the City of Jacksonville, Florida, which planned to construct a regional waste treatment plant in the Arlington East Section. Following the EPA's guidance for site selection, a site was selected; however, public resentment over the selected site, as evidenced by a petition presented by 600 area residents to the EPA, resulted in the EPA requiring the preparation of an environmental impact statement. The time required for the preparation of the EIS is 9-12 months. Jacksonville mayor Hans Tanzler indicated that public involvement would delay the completed project until approximately 1978, two years after the compliance deadline set by N.P.D.E.S. (National Pollutant Discharge Elimination System), which requires the issuing of permits for every direct source of pollutant discharge that now exists or is proposed to exist in the United States. An illustration of cost increases as a result of the EIS process is presented by the Federal Highway Administration (FHA) in the case of the delayed completion of IH-485 in Atlanta, Georgia. The FHA estimated that the cost of the delay in IH-485 construction resulted in cost increases of \$145 968 345.

In addition to the required procedures and reports, there is evidence of inadequate personnel for proper evaluation of Assessment Statements at the EPA. This inadequacy adds time and cost to the EIS process. It is of these delays, costs, and varied agency requirements that government and industry EIS preparers complain. The EIS process as it now exists threatens to break down in a bureaucratic quandary. Environmental Protection Agency records show that for the period June 1 through June 30, 1972, EPA Central and Regional Offices reviewed 142 EIS statements, and that in 69, (about 50% of the EIS statements reviewed) EPA was overdue in its comments (Table 1).

Summing up

One of the major responsibilities of the CEQ is the coordination of the activities of a large number of governmental agencies. The CEQ's success in this regard has been varied and subject to dispute. These coordination activities, however, are important if our nation is to proceed toward its environmental objectives as delineated in the National Environmental Policy Act. Moreover, concern and tangible effort for pollution control are still in early stages of development and the necessary linking mechanisms essential for the effective coordination of a national environmental policy have not yet been fully developed.

As national emphasis shifts toward the enhancement of the environment and containment of pollution, as it must, the coordinative and administrative powers of the CEQ will be appropriately expanded and strengthened to create a strong organizational center essential for effective environmental impact assessment. Additionally, the Environmental Impact Statement, as the primary linking mechanism, will become even more important and pervasive. An effective coordinating board is the only answer to the enforcement of environmental legislation and the solution of pollution problems that are national in scope. The CEQ is the first step toward attainment of that highly desirable goal.

Additional reading

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"Required Statements on Environmental Impact are Stirring Criticism," *Wall Street Journal*, (September 27, 1973), p 1.

Schachter, E. R., "Standards for Evaluating a NEPA Environmental Statement," *Public Utilities Fortnightly*, XC (August 31, 1972), p 29.

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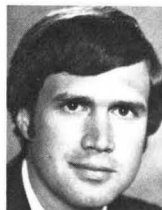
Agriculture-Environmental and Consumer Protection Appropriations for 1974, Hearings Before the House Committee on Appropriations, 93rd Congress, First Session pp 524-525.



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CURRENT RESEARCH

Trace Organic Components as Fingerprints in Gas Chromatographic Identification of Spilled Asphalts

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■ The development and testing of a new concept for oil identification this past year made possible the successful application of gas chromatography to the analysis and identification of asphalts. Through the use of electron capture detection–gas chromatography, the passively labeled perfluorobenzyl thioethers and ethers which are derivatives of weak acids present in trace amounts in discharged heavier petroleum products were separated, and the resulting chromatograms served as fingerprints for identification.

The development and testing of a new concept of oil identification this past year have made possible the first successful application of gas chromatography–electron capture detection to the analysis and identification of asphalts. Asphaltic materials cannot be readily identified to a source by gas chromatography with a flame ionization detector because they are not, by virtue of their high molecular weights and complexity, usually volatile for analysis. The complex, chemical nature of the high molecular weight components of asphalts, their fractionation, and analysis studies are dealt with in annual reviews (1, 2). Bitumen studies using a combination of liquid and gas chromatography (3) disclosed that the gas chromatographic patterns were entirely different for bitumens from Green River shale, Athabasco tar sands, and Niagara dolomite. Most of the gas chromatographic character resides in the saturates fraction.

By means of infrared spectroscopic studies, Beitchman (4), Campbell and Wright (5), and Smith et al. (6) have contributed to the knowledge of asphalt and its changes following oxidation and weathering. In the latter study, asphalts were classified according to geographical producing areas by plotting ratios of certain aliphatic absorption intensities. The ratio method of analysis on a relative basis was discussed by Potts (7).

Using the organic trace components, mercaptans, and phenols contained in petroleum to serve as fingerprints for identification is a relatively new method, which until recently (8) had not been applied toward the identification of petroleum products in surface water.

The novel conversion of weak acids to their respective novel pentafluorobenzyl derivatives and the subsequent EC detection–gas chromatographic analysis of certain effluents have provided technical support in enforcement cases, e.g., tracing of phenols found in the drinking water supply of Wheeling, W.Va. The procedure, developed at the Methods Development and Quality Assurance Research Laboratories, made possible the tracing of phenols found in the city water to its source 20 miles upstream at the parts per billion level (9). This trace amount of phenols was responsible for off-taste in water.

This paper discloses the first successful application of gas chromatography–electron capture detection in the analysis of the organic trace components present in asphalts and its usefulness in providing identification of asphalt pollutants found in surface waters. This, in turn, provides prima facie evidence against suspected polluters. Analytical results obtained by classical methods, metal and elemental analyses, and other newly developed methods of identification, ratios of infrared absorbances (10) and statistical discriminant function analysis (11) are presented to corroborate the electron capture detection–gas chromatographic method.

Experimental

Procedure. *Collection.* The oily, tar-like, spill material was collected by skimming of the water surface with the aid of a clean widemouthed bottle. Source samples were obtained from the asphalt pipe line; all samples were preserved by refrigeration at 5 °C.

Extraction. The water samples (2 g of solid) were extracted with chromatographic grade chloroform (200 ml). Extracts were washed with water, dried over 4 g of sodium sulfate, and filtered. The filtrate was collected in a 300-ml round-bottomed distillation flask.

Concentration. The round-bottomed flask containing the dried chloroform extract was attached to an all-glass distillation setup consisting of a nitrogen ebullator fitted to a Claisen head. The solvent was evaporated off at 200-mm pressure and collected in a glass receiver which led to a dry ice trap and then to the reduced pressure line.

Chloroform removal was monitored by disappearance of infrared absorption bands at 8.22 and 13.20 μ . Extracts of the source material and water samples were treated similarly.

Equipment. *Apparatus.* The operating modes of the Perkin-Elmer 137 and 621 infrared spectrophotometers were given previously (8). Since asphalt petroleum samples are tacky and viscous, thin films were cast from CHCl_3 solution and/or by warming of the asphalt; the final thickness of the film was adjusted so that the minimum transmittance of the peak at 1450 cm^{-1} lay in the range of 5–15%. Traces of chloroform may be monitored by noting the presence or absence of chloroform peaks.

For the electron capture detection–gas chromatographic analysis, a Microtek (Tracor) instrument with a Nickel 63 detector was used initially as described previously (8).

For the “weathered” source and river samples, a Perkin-Elmer gas chromatograph, Model 900, with a Nickel 63 electron capture detector was used. A 10-ft by 0.125-in. stainless steel column containing 1:1 mixture of 5% OV-210 and 5% OV-101 supported on gas chrom Q of 80–100 mesh size was

employed at 175 °C. Argon-methane flow was 30 ml/min. The sensitivity was set at an attenuation of 64, range 10, while the power supply was operated on a pulsed voltage at 100 μ s. The detector temperature was 300 °C. The injector and manifold temperatures were set at 210 °C.

Recorder speed was 5 mm/min, operating at range 5 mV.

Chemicals. Solvents were purchased from Burdick and Jackson Laboratory, Inc., Muskegon, Mich., reagents were of special purity grade. Alpha bromo-2, 3, 4, 5, 6-pentafluorotoluene was purchased from the Aldrich Chemical Co., Inc., Milwaukee, Wis.; it is a lachrymator.

Derivative Preparation and Fractionation on Silica Gel Column. Samples were dissolved in chloroform (250 ml) and extracted three times with a small volume of 5% KOH in 1:1 ethanol-water solution. The alkaline extract was acidified with 5% HCl in water and then extracted with chloroform three times with 35 ml each. The chloroform extract was stirred with 1.0 g of powdered potassium carbonate and then refluxed in the presence of excess pentafluorobenzyl bromide reagent in acetone; 8 ml of reagent solution containing 82 mg/ml, together with 30 ml of acetone, was added. This reagent reacts only with phenols, mercaptans, and organic acids to form the pentafluorobenzyl ethers, thioethers, and esters, respectively. After 1 h of reflux, the solvents were removed at 60 °C/150 mm. Since esters may be hydrolyzed in alkaline solution and removed readily, the residue was again taken up in 100 ml of chloroform and shaken with 15 ml of water to hydrolyze and remove the pentafluorobenzyl esters of the petroleum naphthenic acids. After three washings with 20 ml of water, the pH of the final wash water was 7.

The chloroform layer was dried with anhydrous sodium sulfate and filtered. Solvents were distilled at 60 °C/150 mm. A 100-mg portion of the residue, containing traces of ether and thioether derivatives of phenols and mercaptans from the asphalt source and spill, was fractionated on a 13-cm chromatographic column (12) filled with 34 g of silica gel (Davison 60/80 mesh), using successive 100-ml volumes of hexane, 10% benzene in hexane, 30% benzene in hexane, 50% benzene-hexane, benzene, and ether. Six eluate fractions were collected for analysis by electron capture detection-gas chromatography (Microtek).

Extraction of Weak Acids from Asphalt and Derivative Preparation. The pipeline asphalt (0.5 g) was dissolved in 125 ml of chloroform and water washed vigorously three times with 40 ml of water. This was repeated two times in an attempt to simulate weathering for the source asphalt. Then the remaining weak acid components were extracted with 5% aqueous potassium hydroxide solution (three times 20 ml) and acidified with 3 N HCl. The free weak acids were then taken up with chloroform and converted to the pentafluorobenzyl derivatives in the manner described previously.

The river sample was treated in a similar manner. These residues were not subjected to column chromatographic purification. With the PE 900, 1-2 μ l injections were made.

Results and Discussion

Infrared Analysis. Both of the dried samples collected from the source and the river samples were analyzed with a Perkin-Elmer 137 infrared spectrophotometer. Spectra were characteristically similar throughout the range from 660 to 4000 cm^{-1} . The spectrum of the river sample is shown in Figure 1. Evidence that the source and river samples are similar is demonstrated by infrared ratios taken of the two samples. These ratios are shown in Table I. A plot of the two ratios, 810 cm^{-1} /1375 cm^{-1} vs. 810 cm^{-1} /720 cm^{-1} , obtained on 19 industrial asphalts, designated by solid dots, and 21 No. 6 fuel oils, represented by circles, yields the graphical representation shown in Figure 2. In the transport case, the source

ratio and the spill ratio (squares) lie close together, thus suggesting identity. They are classified as asphalts since they are located within the group of black, solid dots indicating commercial asphalts, manufactured by seven petroleum companies.

Carbon-Hydrogen Analysis. In Table II are shown the carbon and hydrogen determinations of the pipeline asphalt and the Ohio River samples. Values are averages of seven determinations per sample. This agreement between the carbon and hydrogen content of the pipeline asphalt with the Ohio River sample indicates the two samples may be similar. Determinations were made on a Hewlett-Packard 185B, a carbon, hydrogen, and nitrogen analyzer.

Nickel and Vanadium Results. The asphalt samples (0.904 and 1.308 g) were dissolved in an xylene and chloroform (20 + 8) mixture and analyzed by atomic absorption utilizing an HGA graphite furnace (14, 15). The nickel and vanadium contents in the source sample were 39 and 12 $\mu\text{g/g}$; values in the river sample were 43 and 14 $\mu\text{g/g}$, respectively. The nickel

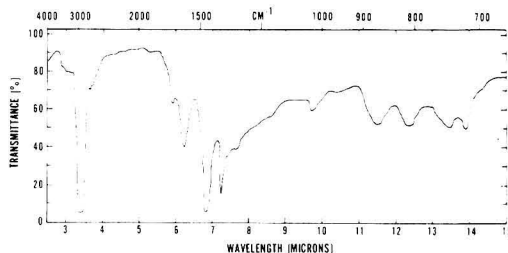


Figure 1. Infrared spectrum of spill asphalt

Table I. Ratios of Infrared Absorbances for Source-River Asphalts

| Ratio absorbances, $\frac{\text{cm}^{-1}}{\text{cm}^{-1}}$ | Asphalt pipeline | Sample found in Ohio River |
|--|------------------|----------------------------|
| $\frac{720}{1375}$ | 0.32 | 0.32 |
| $\frac{810}{1375}$ | 0.28 | 0.29 |
| $\frac{810}{720}$ | 0.86 | 0.89 |
| $\frac{1600}{1375}$ | 0.89 | 0.83 |
| $\frac{1600}{720}$ | 2.76 | 2.53 |

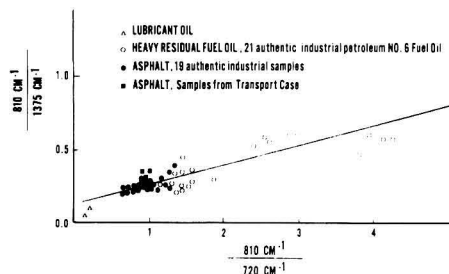


Figure 2. Relationship of spill and source asphalt among 40 commercial asphalts and No. 6 fuel oils involving two RIA's

Table II. Analysis of Source–River Asphalts

| Parameters | Asphalt from pipeline | Sample from Ohio River |
|---------------------------|-----------------------|------------------------|
| Carbon content, % | 85.57 | 86.07 |
| Hydrogen content, % | 10.86 | 11.16 |
| Asphaltene, % | 21.1 | 22.6 |
| Nickel, $\mu\text{g/g}$ | 39 | 43 |
| Vanadium, $\mu\text{g/g}$ | 12 | 14 |
| Za | -5.22735 | -4.68050 |
| Zo | -8.40503 | -8.92630 |

and vanadium in the river sample appear to be somewhat higher than the source sample, but results are in good agreement (see Table II). Nickel and vanadium could be higher in value for the water samples if hydrocarbons are lost during weathering in water. The vanadium–nickel ratios for the pipeline and for the river sample are 0.31 and 0.33, respectively.

Asphaltene Content. The asphaltene content, determined by the procedure described by Abrahams (13), indicates that source and spill petroleums have similar asphaltene content (as shown in Table II).

Data Treatment and Statistical Analysis. Infrared spectrophotometry has been a useful technique for the characterization and identification of these heavy materials. With the use of a combination of infrared spectrophotometry, data treatment, data transformation, and discriminant function analysis with computer assistance, a precise method of classification has been derived (11). From among 19 samples of commercial asphalts and 21 No. 6 fuel oils, the unknown river sample was linked to the commercial source via good agreement of mathematical values from corresponding linear discriminant functions as indicated by the Za values in Table II. Za and Zo are the linear discriminant function values of asphalt and heavy residual fuel oil, respectively. The higher algebraic values belong to the Za's. Therefore, as shown by Kawahara et al. (11), the unknown river and manufacturing source samples were identified as asphalts. In addition, the fairly close agreement of the higher algebraic function values of asphalts (Za's) of the source and spill asphalt suggests possible identity.

Gas Chromatographic Analysis. The following demonstration is proof that the Ohio River sample is similar to the source sample taken from the asphalt pipeline. To demonstrate their similarity, the weak acid components (mercaptans and phenols) of the asphalts taken from the source and from the river were compared, via inspection of the electron capture detection gas chromatograms. Each asphalt sample was converted to the pentafluorobenzyl derivatives and fractionated into six portions using solvent mixtures of varying polarity to effect a separation on the silica gel column. The third eluate fraction yielded the revealing electron capture detection gas chromatograms (Figures 3 and 4), representing the source and spill asphalts, respectively.

The other fractions were nondescriptive or showed only a few peaks. In the latter cases, the gas chromatogram patterns were similar, but the third eluate represented the major fraction. The retention times of the 14 resolved peaks, taken from the electron capture detection–gas chromatographic analysis of the pentafluorobenzyl derivatives of the asphalt pollutant from the Ohio River (Figure 4), were compared to those from resolved peaks of the derivative asphaltic material that was taken from the asphalt pipeline (Figure 3). Fourteen peaks (mercaptans and phenols) of the source sample have the same retention times as 14 peaks (mercaptans and phenols)

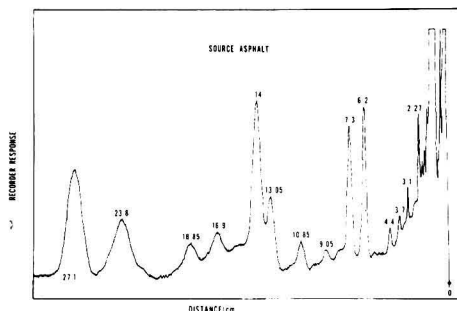


Figure 3. Electron capture detection gas chromatogram of derivatives of weak acids from source asphalt

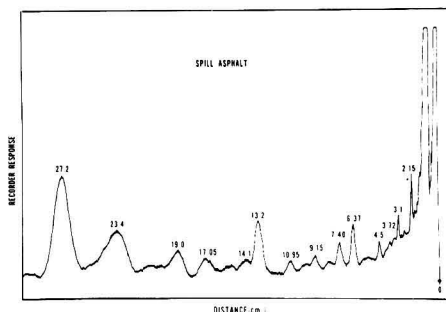


Figure 4. Electron capture detection gas chromatogram of derivatives of weak acids from spill asphalt

Table III. Electron Capture Detection–Gas Chromatography Retention Distances of Asphalt Derivatives

| Pipeline sample | River sample |
|-----------------|--------------|
| 2.27 | 2.15 |
| 3.10 | 3.10 |
| 3.70 | 3.72 |
| 4.40 | 4.50 |
| 6.20 | 6.37 |
| 7.30 | 7.40 |
| 9.05 | 9.15 |
| 10.85 | 10.95 |
| 13.05 | 13.20 |
| 14.00 | 14.10 |
| 16.90 | 17.05 |
| 18.85 | 19.00 |
| 23.80 | 23.40 |
| 27.10 | 27.20 |

of the pollutant Ohio River sample. Table III shows the excellent agreement between the 28 retention times of the derivative peaks. (Three components of the 14 found in the source sample are larger in amount than the corresponding weak acid peaks found in the river sample; these may be lost possibly by solubilization, etc.)

This supposition was verified by analyzing the weak acid derivatives of the water-washed pipeline asphalt. Results obtained demonstrate that the “spill” river asphalt was derived from the pipeline asphalt. Figure 5 shows that the

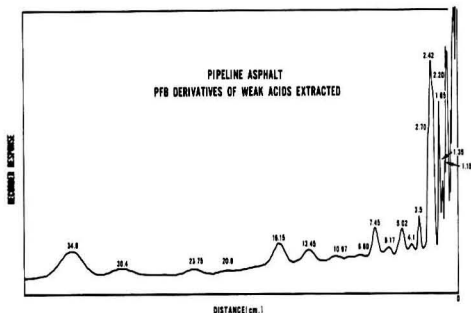


Figure 5. Electron capture detection gas chromatogram of derivatives of weak acids extracted from source asphalt washed vigorously

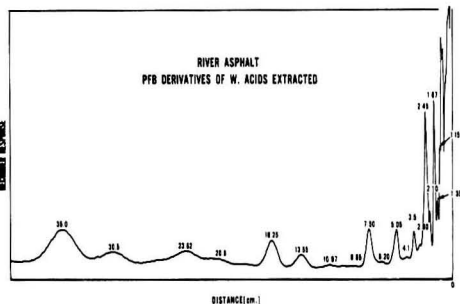


Figure 6. Electron capture detection gas chromatogram of derivatives of weak acids extracted from river asphalt

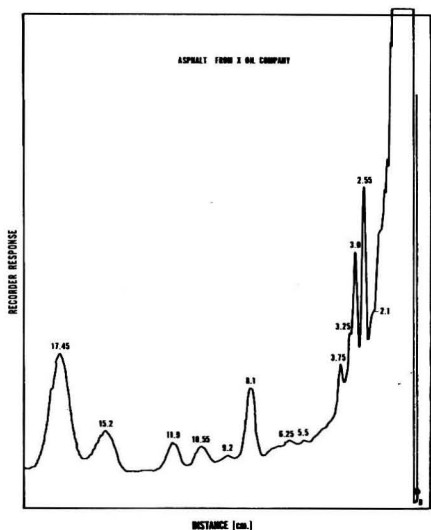


Figure 7. Electron capture detection gas chromatogram of derivatives of weak acids of asphalt from X oil company

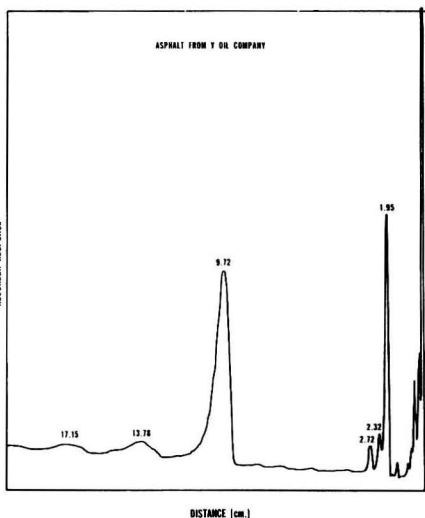


Figure 8. Electron capture detection gas chromatogram of derivatives of weak acids of asphalt from Y oil company

electron capture detection gas chromatogram of the weak acid derivatives from the artificially weathered asphalt obtained from the pipeline is similar to the EC detection gas chromatogram of the weak acid derivatives removed from the river asphalt (Figure 6). A slight quantitative variation appears in a few of the minor peaks of the river sample. The two shoulders of the 2.4-cm peak indicate some differences in amount. All retention values coincide.

The two asphalts are the same since mercaptans (and phenols) contained in the source sample asphalt match very closely the mercaptans (and phenols) contained in the spill asphalt. (Other asphalts were compared and showed different electron capture detection gas chromatograms.) Figures 7 and 8 are electron capture detection gas chromatograms of the pentafluorobenzyl derivatives of weak acids extracted from two different asphalts received from two oil companies. One sample contains larger amounts of the lower boiling weak acids whose derivatives are emitted in the first 1.5 cm. The remaining peaks appear to contain smaller amounts of the higher boiling weak acid derivatives in comparison to the asphalt samples in the present case. The ECD-GC pattern of the other asphalt sample is quite different. The two chromatograms were taken under similar operating conditions.

All results indicated that the pipeline asphalt was the source of the pollutant river asphalt.

Conclusions

This study has been successful in that a novel method of using weak acids to fingerprint heavy petroleum oils, to trace them to the source, was discovered. A new derivative preparation followed by electron capture detection-gas chromatography was used to exclude measurement of unwanted impurities that usually plague flame ionization detection. In addition, the weathering of asphalts may be simulated by the simple process of vigorous water washing.

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Internal Diffusion and Reaction in Biological Films

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■ A theoretical model describing diffusion of substrate within the film matrix and simultaneous zero-order substrate consumption adequately explains the experimental observations reported in this and other similar investigations. This model predicts that substrate removal is directly proportional to film thickness up to a critical value corresponding to the depth of substrate penetration in the film. Beyond this thickness, substrate removal remains constant. With the catalyst effectiveness factor model, it is possible to quantitatively evaluate the magnitude of internal diffusion resistances which make the observed rate less than the maximum possible.

When analyzing the different factors that affect the rate of substrate utilization by biological films, it is convenient to simplify all the steps occurring in the overall process into three major ones:

- (a) Diffusion of substrate from the bulk of the liquid to the interface between the liquid and the biological film
- (b) Diffusion of substrate within the porous biological slime
- (c) Biochemical reaction (substrate consumption) within the film.

In the analysis that follows, it is assumed that the diffusion of the reaction products from the internal pores of the biomass to the outer surface of the film has no effect on the rate of substrate utilization. This assumption is supported by the fact that since the reaction is irreversible, its rate cannot be affected by the concentration of products unless they accumulate in excessive amounts in the environment. On the basis of this rationale, the investigation reported here only considered steps a through c above.

Steps b and c take place simultaneously and thus mutually interfere; the overall phenomenon resulting from these two steps takes place in series with step a, so that the rates of both the overall phenomenon and step a have to be equal under steady-state conditions. A proper identification of each one of these processes is required to understand and adequately model the kinetics of the substrate uptake reaction by biological films.

The external mass transfer process (step a) has been examined in detail elsewhere (1). The effect of fluid velocity on the overall process was studied, and the reaction-controlled regime was experimentally defined.

The subsequent analysis, which concentrates on the simultaneous internal diffusion and substrate consumption process, will assume that external diffusional resistances have been eliminated with a suitable choice of fluid velocity. In this way the overall process will not be controlled by the rate of transfer of substrate from the liquid bulk to the film surface, and the true kinetics of the reaction can be observed.

Internal diffusion and simultaneous substrate consumption in biological flocs were dealt with in detail by Mueller (2) and Bailod (3, 4). These investigators clearly demonstrated that at low oxygen concentrations or at low carbonaceous substrate concentrations, the rate of uptake was strongly influenced by internal diffusion.

With regard to biological films, several investigators (5-8) have treated the film as a reactive surface rather than as a porous matrix. Others (9-11), dealing with diffusion and oxygen consumption, have treated the film as a homogeneous mass. However, when dealing with carbonaceous substrates, the analyses of the same phenomena have been restricted to qualitative descriptions of the effects of film thickness on the uptake rate (12-16).

Kornegay and Andrews (12) confirmed the observations of Sanders (13) and Tomlinson and Snaddon (14) that once a certain film thickness is exceeded, the removal of substrate is not increased by further accumulation of microorganisms on the slime. These experimental observations were further substantiated by Hoehn (15, 16) using a synthetic medium (see Figures 1 and 2). He attributed the observed reduction in substrate uptake per unit film volume, when films have reached some limiting thickness, to changes in the total community metabolism imposed by oxygen depletion in the deeper layers of film.

Even though there is sufficient evidence about the relationship between the uptake rate and film thickness (Figures 1 and 2), to the writer's knowledge, there is no mathematical model which predicts the observed behavior. Considering that internal diffusional resistances significantly affect the rate of substrate removal by biological flocs, an analysis of internal diffusion in films may provide a satisfactory explanation to the behavior depicted in Figures 1 and 2. Therefore, one of the objectives of the investigation reported herein is to establish a mathematical description of the rate of substrate removal by biological films and its relationship with film thickness.

Theoretical Considerations

In the subsequent analysis a porous-catalyst model will be used to represent the diffusion and reaction phenomena occurring in a biological film.

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Simultaneous diffusion and reaction in this model (see Figure 3) can be analyzed by writing the continuity equation (17) on substrate which, neglecting the convective terms, can be written as follows:

$$\frac{\partial S}{\partial t} = D_{\text{eff}} \nabla^2 S + r_v \quad (1)$$

S = substrate concentration at any point within the film

t = time

D_{eff} = effective diffusivity of substrate S in the film

r_v = rate of substrate consumption per unit film volume

In using this equation, the assumption is being made that the biological slime consists of a gel throughout which the microorganisms are uniformly scattered. In other words, the biochemically active reaction sites are assumed to be distributed in the gelatinous mass in a similar way as in a porous catalyzed gel.

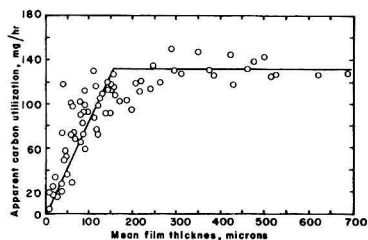


Figure 1. Rate of carbon utilization as function of film thickness [Hoehn (15)]

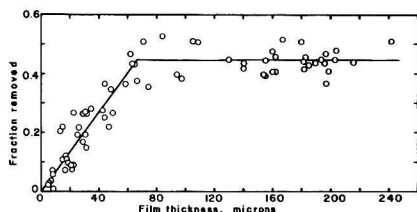


Figure 2. Fraction of glucose removed as function of film thickness [Kornegay and Andrews (12)]

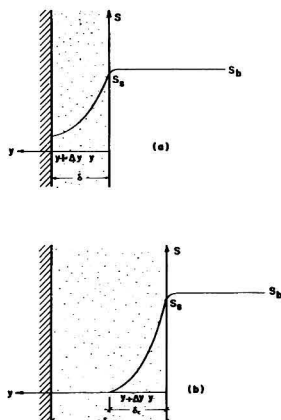


Figure 3. Concentration distribution within biological film under complete substrate penetration (a) and incomplete substrate penetration (b)

An implication of this assumption is that the film volume should be directly proportional to the film active biomass. Data supporting this relationship are presented elsewhere (1).

The effective diffusivity used in Equation 1 represents a bulk diffusion coefficient, based on the total cross section of slime normal to the direction of diffusion. It is defined as the ratio of the flux of substrate (perpendicular to the film surface) to the concentration gradient, and must be measured experimentally. No attempt was made in this study to determine the actual mechanism for diffusion within the pores of the biological slime. However, experimentally determined values of D_{eff} will be presented later.

Since the geometry being analyzed in planar, only the diffusion occurring in the direction normal to the surface needs to be considered. Furthermore, after a certain time, a stationary concentration distribution is established, and steady-state conditions can be assumed. These simplifications lead to the expression:

$$D_{\text{eff}} \frac{d^2 S}{dy^2} = r_v \quad (2)$$

The solution of Equation 2 for the general case of an n th order reaction has been presented by Frank-Kamenetskii (18). For the case of the substrate consumption reaction, there is sufficient experimental evidence that for all practical substrate concentrations, the true rate is zero order (4, 19-24). With this assumption Equation 2 can be written as follows:

$$\frac{d^2 S}{dy^2} = \frac{k_p}{D_{\text{eff}}} \quad (3)$$

where k_p is the true rate of substrate uptake (a constant), $\text{mol}\cdot\text{s}^{-1}\cdot(\text{cm}^3 \text{ film})^{-1}$.

The boundary conditions associated with Equation 3 depend on whether there is complete substrate penetration within the film (Figure 3a) or incomplete penetration (Figure 3b). In the first case, the boundary conditions are

$$\text{at } y = 0, S = S_b \quad (4)$$

$$\text{at } y = \delta, \frac{dS}{dy} = 0 \text{ (no penetration at the wall)} \quad (5)$$

On the other hand, when substrate is depleted within a distance δ_c , which is less than the film thickness, δ , boundary condition 5 must be modified as follows:

$$\text{at } y = \delta_c, \frac{dS}{dy} = 0 \text{ (no mass transport beyond } y = \delta_c) \quad (6)$$

Integration of Equation 3 with boundary conditions 4-6 yields the concentration gradient, dS/dy . The rate of substrate consumption, in mol/s , can be found by recognizing that the reaction rate equals the rate of mass transfer across the film surface; the latter can be defined in terms of Fick's first law of diffusion. The rate expressions which result from this analysis are the following:

In the case of complete substrate penetration (Figure 3a),

$$r = A \cdot k_p \cdot \delta, \text{ mol/s} \quad (7)$$

and in the case of incomplete substrate penetration (Figure 3b),

$$r_p = A(2 D_{\text{eff}} k_p)^{1/2} (S_b)^{1/2}, \text{ mol/s} \quad (8)$$

According to Equation 7, the observed reaction kinetics are the true zero-order kinetics assumed to occur within the film. This true reaction rate is commonly termed "intrinsic" reaction rate (25, 26). On the other hand, Equation 8 shows an important point usually overlooked in the environmental engineering literature dealing with films (5-8), i.e., even though the depth of penetration may be small as compared

with the entire film thickness, the effect of internal diffusion resistances is to mask the true zero-order kinetics yielding an apparent reaction order of $1/2$. The observed reaction order of an n th order reaction significantly affected by pore diffusion is $(n + 1)/2$ (27). Thus, kinetic information gathered under conditions of significant pore diffusion can lead to erroneous conclusions unless proper account is made for pore diffusion effects. This apparent or observed rate of the reaction has been termed the "macroscopic" rate (18).

The depth of penetration of substrate S within the bio-film is given by

$$\delta_c = \left(\frac{2 D_{\text{eff}} S_s}{k_v} \right)^{1/2} \quad (9)$$

If Equation 9 is combined with Equation 8, the following result is obtained

$$r_p = A \cdot k_v \cdot \delta_c \quad (10)$$

Equation 10 illustrates an important point, that is, when there is incomplete substrate penetration (in the case of thick films), the observed rate depends on the magnitude of the depth of penetration, and it is independent of the total film thickness.

It is now interesting to try to quantitatively evaluate the magnitude of the internal diffusional resistances. This can be achieved by using the effectiveness factor, a concept which is extensively used in heterogeneous catalysis.

Evaluation of Internal Diffusional Resistances. Effectiveness Factor. The concept of the catalyst effectiveness factor could be applied to the case of biological films. With the definition given in the literature (26, 28, 29), the effectiveness factor will be given by

$$\eta = \frac{r_p}{r} \quad (11)$$

When there is incomplete substrate penetration, substitution of Equations 7 and 10 in Equation 11 gives

$$\eta = \frac{\delta_c}{\delta} \quad (12)$$

This equation defines the fraction by which one should multiply the intrinsic rate to obtain the observed rate; its role is that of a correction factor to account for internal diffusional resistances.

For the case of a thin film in which there is complete substrate penetration, the effectiveness factor is unity since both the observed and the intrinsic rates are equal.

From the previous analysis, it is reasonable to predict that during the growth cycle of a biological film, two stages will occur. First, during the accumulation of the first layers of microorganism, the intrinsic rate will be observed, following Equation 7, and the effectiveness factor will be 1.0. Second, when a critical film thickness is exceeded, the substrate does not penetrate to the inner boundary, and the effectiveness factor will progressively decrease following Equation 12. Under these conditions the intrinsic rate is no longer observed, internal diffusion affects the rate of substrate removal, and Equation 8 must be used.

Prediction of Performance of Continuous-Flow Laboratory Reactor. The kinetic analysis presented above was tested with a laboratory reactor described elsewhere (1). Briefly, it consisted of two concentric cylinders of different diameter, the inner one being stationary, and the outer rotating around its axis. A glucose solution flowed continuously through the annular space at a rate of 100 ml/min; the concentration of glucose in the influent stream was given several values (from 2 to 200 mg/l.) to test the effect of this parameter on the rate of film accumulation. A biological film grew adhered to the walls of the cylinders, and its thickness was measured by sampling the cylinder walls by means of plastic

slides and plugs. Operation of the system in the kinetic regime was possible by using high rotational speeds (linear wall velocity greater than 0.8 m/s) set by means of a speed controller. Turbulent flow conditions prevailed throughout this investigation.

A simple mass balance on substrate yields the following expressions describing the fraction of substrate removed:

If pore diffusion effects are negligible, i.e., if $\eta = 1.0$,

$$x = \frac{k_v A}{Q S_i} \cdot \delta \quad (13)$$

x = fraction of substrate removed

$$= 1 - S_e/S_e$$

S_i = influent substrate concentration, mol/cm³

S_e = effluent substrate concentration, mol/cm³

Q = volumetric flow rate, cm³/s

On the other hand, when pore diffusion effects are significant, i.e., $\eta < 1.0$,

$$x = \frac{2}{1 + \left[1 + 2 \left(\frac{Q}{A} \right)^2 \frac{S_i}{D_{\text{eff}} \cdot k_v} \right]^{1/2}} \quad (14)$$

According to Equations 13 and 14, a plot of substrate removal vs. film thickness will yield two straight lines, the first (corresponding to Equation 13), a line through the origin with slope $k_v A/Q S_i$, and a second (corresponding to Equation 14), a horizontal line. Such a plot is presented in Figure 4, along with Kornegay's experimental observations. The zero-order model described in this paper provides an adequate theoretical explanation for the observations reported in the literature (12, 15, 16).

The value of the effective diffusivity, D_{eff} , can be readily obtained from a plot such as that in Figure 4. The horizontal line, described by Equation 14, provides the numerical value of the equilibrium conversion characteristic of the system. Hence, solving for D_{eff} , the following expression is obtained:

$$D_{\text{eff}} = \frac{S_i \left(\frac{Qx}{A} \right)^2}{2 k_v (1 - x)} \quad (15)$$

Equations 13 and 14 were also tested with the observations gathered during the experiments performed with the rotating-cylinder reactor. These results are presented in the following section.

Experimental Approach

The overall experimental plan included the following phases (1):

- (a) Effect of rotational speed on turbulent mass transfer
- (b) Study of pore diffusion and simultaneous glucose consumption

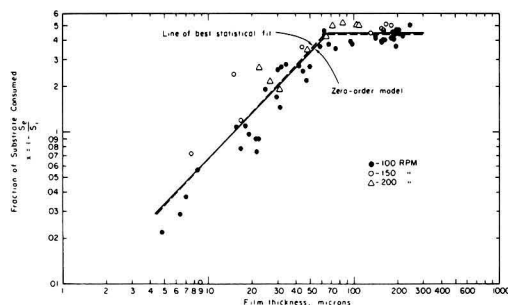


Figure 4. Plot of Kornegay and Andrews' data (12) corresponding to $S_i = 1.24 \times 10^{-6}$ mol/cm³ (224 mg/l.), showing zero-order model described by Equations 13 and 14

(c) Effect of influent substrate concentration on the rates of substrate uptake and film growth.

The results of the first experimental phase, which are reported separately (1), defined the conditions under which the reactor would be operated under reaction-controlled conditions. Phase c is reported elsewhere (30).

The experiments of phase b were carried out using both low and high glucose concentrations to determine if the two-line pattern described previously (see Figure 4) could be confirmed. Three different low glucose concentrations, namely, 1.23×10^{-8} , 1.79×10^{-8} , and 2.89×10^{-8} mol/cm³ (2.2, 3.2, and 5.2 mg/l.) were used with two different size reactors. With each of these concentrations, a run was started by eliminating the excess of a well-acclimated slime which had been previously grown, so that a 2–5- μ layer was obtained. Then, the film was allowed to grow continuously using high rotational speeds so that the system was not controlled by external diffusion. Samples of influent and effluent streams were collected two or three times daily, and the film thickness was measured with a stage microscope every time a liquid sample was taken. The run was usually stopped after 60 h, yielding approximately from four to six useful data points.

To maintain aerobic conditions in all runs during the experiments performed in the low concentration range, aeration of the influent with plain air was sufficient. However, when the glucose concentration was increased to 1.11×10^{-6} mol/cm³ (200 mg/l.), aeration with pure oxygen was necessary to avoid anaerobic conditions in the reactor contents.

Results and Discussion

Figures 5 and 6 show the results of the experiments performed with low glucose concentration (5.2 mg/l.) and high glucose concentration (200 mg/l.). The zero-order model described by Equations 13 and 14 provides a satisfactory relationship between the fraction removed and the film thickness.

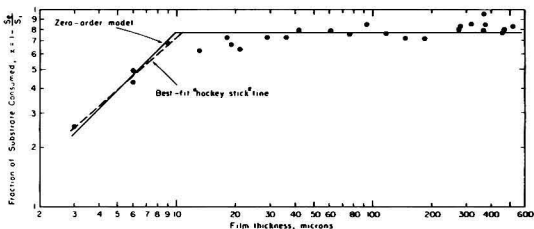


Figure 5. Effect of film thickness on fraction of glucose removed when $S_i = 2.89 \times 10^{-8}$ mol/cm³ (5.2 mg/l.)

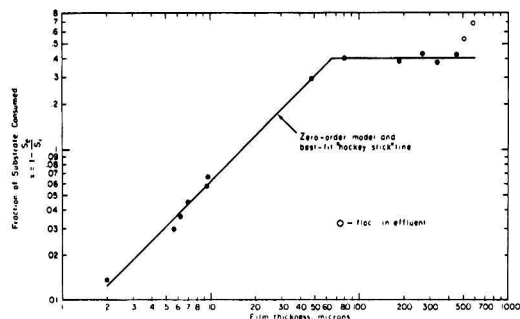


Figure 6. Effect of film thickness on fraction of glucose removed when $S_i = 1.11 \times 10^{-6}$ mol/cm³ (200 mg/l.)

The experimentally observed values of effectiveness factor were also computed in each case by dividing the macroscopic rate (observed when $\delta > \delta_c$) by the average intrinsic rate ($r_v = R_v$), which is observed when $\delta < \delta_c$. The theoretical model, described by Equation 12, namely

$$\eta = \frac{\delta_c}{\delta} \quad (12)$$

predicts that a plot of η vs. δ on log-log paper should yield two straight lines, a horizontal ($\eta = 1.0$) for $\delta < \delta_c$, and an inclined one (slope = -1.0) for $\delta > \delta_c$. Such lines are presented in Figures 7 and 8 along with the experimental observations; they provide a good fit for the experimentally observed effectiveness factors, supporting again the zero-order model described in this paper.

A summary of the values of D_{eff} computed from Equation 15 for all the experiments carried out by the writer and for those of Kornegay and Andrews is presented in Table I which also contains the values of the depth of penetration solved from Equation 13.

The effective diffusivities reported in Table I seem to be reasonable. If they are compared with the molecular diffusivity of glucose in water at the same temperature, i.e., $D_s = 6.4 \times 10^{-6}$ cm²/s (31), they vary from 19.5 to 50.5% of the latter, a representative value being 44% (average $D_{eff} = 2.83 \times 10^{-6}$ cm²/s).

A point worth noting is that the results of this investigation when $S_i = 200$ mg/l. substantially agree with the results of an independent work (12) performed under similar conditions.

Summary and Conclusions

Substrate removal is directly proportional to film thickness when thickness is less than a critical value, and once this value is exceeded, removal no longer depends on film thickness. These observations were confirmed with a continuous film

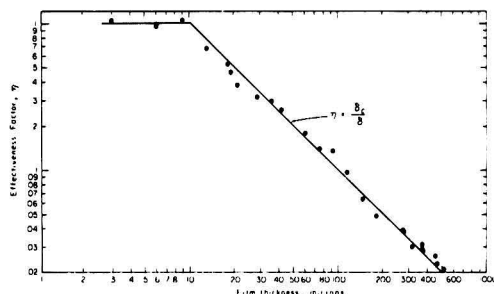


Figure 7. Plot of observed effectiveness factor vs. film thickness. $S_i = 2.89 \times 10^{-8}$ mol/cm³ (5.2 mg/l.)

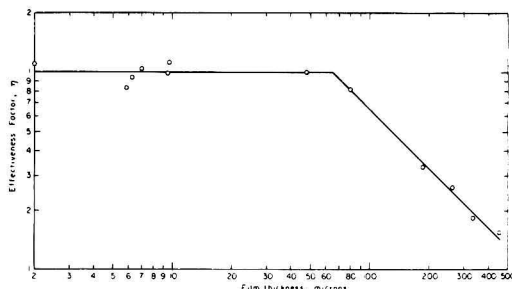


Figure 8. Plot of observed effectiveness factor vs. film thickness. $S_i = 1.11 \times 10^{-6}$ mol/cm³ (200 mg/l.)

culture apparatus at both low and high substrate concentrations.

The theoretical analysis of simultaneous internal diffusion and reaction within the film matrix, assuming zero-order intrinsic kinetics, provides a satisfactory explanation for the observations reported here and those reported in the literature. This analysis provides two rate expressions which must be applied depending on the magnitude of the film thickness. The first, Equation 7,

$$r = A \cdot k_v \cdot \delta, \text{ mol/s}$$

gives the rate of consumption of substrate, provided there is complete substrate penetration within the film. This occurs during the early stages of film growth until a film thickness, given by Equation 9,

$$\delta_c = \left(\frac{2 D_{\text{eff}} S_s}{k_v} \right)^{1/2}$$

is exceeded.

The second rate expression applies to the case of incomplete substrate penetration, in which internal diffusion effects are significant. In this case the macroscopic rate is given by Equation 8,

$$r_p = A [2 D_{\text{eff}} k_v (S_s)]^{1/2}, \text{ mol/s}$$

which is a half-order reaction with respect to substrate concentration. Thus, if pore diffusion effects are neglected when investigating the kinetics of substrate uptake by films, the conclusions arrived at, regarding the reaction order, will be inaccurate.

Both Equations 7 and 8 can be used in modeling a fixed-film biological reactor. However, these equations do not include the effect of the influent substrate concentration on the magnitude of the intrinsic uptake rate, k_v . These effects are discussed separately (30) and must be taken into account.

Internal diffusional resistances can adequately be evaluated by using the catalyst effectiveness factor. The results indicate that this factor decreases with increasing film thickness; therefore, the macroscopic rate will be less than the intrinsic rate for all cases of film thickness greater than the critical value.

Nomenclature

- A = total film external area, cm^2
 D_s = molecular diffusivity of substrate, $\text{cm}^2 \text{s}^{-1}$
 D_{eff} = effective diffusivity, $\text{cm}^3 \text{ fluid cm}^{-2} \text{ film s}^{-1}$
 N = rate of mass transfer, $\text{mol s}^{-1} \text{ cm}^{-2}$
 N_{AZ} = flux of substance A in the z -direction, $\text{mol s}^{-1} \text{ cm}^{-2}$
 Q = volumetric flow rate, $\text{cm}^3 \text{ s}^{-1}$

r = intrinsic rate of substrate removal, mol s^{-1}

r_p = macroscopic or observed rate of reaction, mol s^{-1}

r_v = intrinsic reaction rate per unit film volume, $\text{mol s}^{-1} \text{ cm}^{-3} \text{ film}$

S = concentration of substrate, $\text{mol cm}^{-3} \text{ fluid}$

S_e = substrate concentration in the effluent, $\text{mol cm}^{-3} \text{ fluid}$

S_i = substrate concentration in the influent, $\text{mol cm}^{-3} \text{ fluid}$

S_s = concentration of substrate at film surface, $\text{mol cm}^{-3} \text{ fluid}$

x = fraction of substrate removed, dimensionless

y = coordinate normal to film surface, cm

δ = thickness of biological film, cm

δ_c = depth of penetration of substrate within film matrix, cm

η = effectiveness factor, dimensionless

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Table I. Observed Values of Effective Diffusivity and Depth of Penetration of Glucose in Biological Films

| Av influent glucose concn, mg/l. | No. of observations on which D_{eff} based | Effective diffusivity, ^a $10^6 \text{ cm}^2/\text{s}$ | Depth of penetration, μ |
|----------------------------------|---|--|-----------------------------|
| 2.2 | 5 | 4.31 | 12.2 |
| 3.0 | 13 | 4.86 | 16.0 |
| 5.2 | 2 ^b | 1.25 | 12.4 |
| 5.2 | 22 | 1.88 | 10.2 |
| 19.8 | 2 | 2.25 | 19.7 |
| 200.0 | 5 | 2.46 | 65.1 |
| 224.0 ^c | 33 | 2.93 | 66.6 |

^a Temperature = 22 °C. Average effective diffusivity observed in this investigation. $D_{\text{eff}} = 2.83 \times 10^{-6} \text{ cm}^2/\text{s}$. ^b Observed during external diffusion experiments. ^c Kornegay and Andrews' experiments.

Chlorinated Hydrocarbon Pesticides in Western North Atlantic Ocean

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■ Both DDE and dieldrin are detected in the offshore waters of the western North Atlantic Ocean from the surface to 1000 m depth. The mean concentrations of the two pesticides are 3.8 (DDE) and 5.8 (dieldrin) parts per trillion (ng/l.). Other chlorinated pesticides (lindane, aldrin, DDD, and DDT) could not be detected, at most sample sites, by currently available analytical techniques. The data suggest that considerable variability, both with depth and distance from shore, is a dominant feature of the distribution of chlorinated pesticides in the North Atlantic Ocean. Concentrations of DDE and dieldrin range from 0.1 to 18.1 and 0.4 to 19.4 ng/l., respectively. The observed environmental distribution of these pesticides would be consistent with an hypothesis of uptake and transport of these compounds on particulates in the sea.

Although the presence of various chlorinated hydrocarbons in oceanic biota has been well documented (1-4), the occurrence and concentration of these compounds in seawater itself have only recently been reported (5-7). These reports suggest that polychlorinated biphenyls (PCB), and to a lesser extent DDT, are widespread contaminants of the North Atlantic Ocean. However, even with these reports, very limited data are available concerning the distribution of chlorinated hydrocarbons in the sea. The present paper is a report of the distribution and concentration of DDT [1,1-bis-(*p*-Chlorophenyl)-2,2,2-trichloroethane], DDD [1,1-bis-(*p*-Chlorophenyl)-2,2-dichloroethane], DDE [1,1-bis-(*p*-Chlorophenyl)-2,2-dichloroethylene], dieldrin (1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethano-naphthalene), aldrin (1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo-exo-5,8-dimethano-naphthalene), and lindane (1,2,3,4,5,6-Hexachlorocyclohexane) with depth and distance from shore in the North Atlantic Ocean.

Despite current bans on the use of certain hazardous substances (i.e., the DDT ban and limitations on the use of PCB in the United States), the ever-increasing worldwide use of industrial and agricultural chemicals, as part of the effort to combat hunger and disease, continues to assault the biosphere with persistent toxic compounds. Considerable quantities of chlorinated hydrocarbons find their way into the world's oceans, primarily by the atmospheric route (4, 8). There, they are acted upon by a myriad of physical and biological forces which eventually lead to the dispersal of these compounds in the sea. Knowledge of this distribution pattern is significant in that we might better trace the fate of important biospheric pollutants, determine what effects they may have on marine organisms, and gain insight into the complex forces acting to distribute compounds within the sea.

Recent data of Harvey et al. (7) suggest that the concentration of at least one class of these compounds, PCB, has decreased dramatically (40X) in North Atlantic surface waters since 1972. This reduction has followed a decline in certain industrial applications of PCB. These authors present some arguments which support the hypothesis that PCB associated with sedimenting particulate matter can account for the observed rapid decline in surface PCB concentrations.

Experimental

Water samples were collected from the western North Atlantic Ocean between May 31, 1972, and June 13, 1972, during cruise E-8B-72 of the *R. V. Eastward*. Samples were collected by means of either a diethyl ether washed bucket (for surface samples) or 10-l. polyvinylchloride Niskin bottles. Samples were obtained from the surface, 50, 500, and 1000 m depth. Figure 1 shows a chart of the cruise route and sample stations, which are numbered according to the standard *R. V. Eastward* continuous station numbers. Surface samples only were obtained from the three westernmost stations. The samples were stored in the dark in 6-l. ether-washed polyethylene jerricans which were taken to the University of North Carolina, Department of Environmental Sciences and Engineering, for extraction and subsequent analysis.

Reagents. Reagents used were diethyl ether, pesticide grade; hexane, pesticide grade; and sodium sulfate, anhydrous, granular, AR grade washed in diethyl ether before use.

Extraction. Samples were extracted with boiling ether in 2-l. continuous extraction chambers. In each case 1.8 l. of seawater was extracted for 4 h. This procedure was chosen since continuous extraction is a more reproducible method than traditional separatory funnel extractions (9, 10). The ether extract was dried over anhydrous sodium sulfate which had been previously extracted with pesticide grade ether. This latter procedure was necessary since the sodium sulfate was contaminated with a substance which produced gas chromatographic peaks very similar to those produced by the PCB Arochlor 1254. Ether washing eliminated this problem. To be certain that no part of the system was causing further contamination, all glassware was washed with ether and periodically tested for interfering contaminants. (Several containers of diethyl ether, AR grade, were also contaminated with compounds yielding chromatograms very similar to Arochlor 1254. Unlined plastic caps appeared to be the source of the contamination.) This testing revealed no further contamination problem. The volume of the ether extract was then reduced to a few drops under reduced pressure in a rotary evaporator, and the residue suspended in hexane. Pesticide concentrations in the extracts were then determined by Ni-63 electron capture gas chromatography.

Gas Chromatographic Parameters. Instrument: Perkin-Elmer Model 900 (The Perkin-Elmer Corp., Norwalk, Conn. 06856). Column: glass, circular, 6 ft (1.8 m) × 0.25 in. (0.64 cm) o.d. × 0.08 in. i.d. (0.20 cm), packed with 3% OV-1 and 7% OV-210 (combined liquid phase) on 60/80 mesh acid washed Chromosorb W; all column packings were conditioned by baking with gas flow for five days at 250 °C. Detector: Nickel 63 electron capture operated in pulse mode (50 V for 1 μs). Carrier gas: nitrogen (zero gas grade), 80 ml/min. Thermal parameters: column temperature, programmed 165-180 °C, 4 °C/min, 6-min initial time, 12-min final time; injector temperature, 200 °C; manifold temperature, 240 °C; detector temperature, 270 °C.

The procedure for the analysis of chlorinated hydrocarbons in water is well known (11). In the present case, however, the procedure was modified in two ways. First, nitrogen, was employed as the carrier gas in pulse mode electron capture gas chromatography. Additionally, the temperature programming capability of the GC was utilized with the electron capture

detector. These modifications, in combination with the liquid packing employed, provided for adequate separation of all the compounds under study. Figure 2 shows (A) a typical chromatogram of a standard mixture of the six chlorinated hydrocarbons and (B) a sample chromatogram (station 20129, 1000 m depth). Tests with the PCB Arochlor 1254 and chromatograms of other PCB mixtures (12) suggest that there are no compounds of PCB origin which interfere with DDE and dieldrin peaks under the conditions employed in this study. Although DDT and DDD might still be confused with chlorinated biphenyls of PCB origin, these evaluations increase confidence in the qualitative identification of DDE and dieldrin.

Samples were analyzed on two additional columns to aid in confirming the identity of the observed peaks. Peaks with retention times corresponding to the same pesticide standards were observed when ocean water extracts were injected on a DC-200 (5%) and an SE-30 (5%) column in addition to the

analytical column. The observed pesticide concentrations were not sufficient to allow the use of combined gas chromatography-mass spectrometry as a supplementary identification tool.

Blank values for the handling and storage conditions were determined by holding distilled, deionized, carbon filtered water in polyethylene jerricans which were subsequently extracted and analyzed as the seawater samples. Reported data have been corrected for blank values of 0.7 ng/l. for DDE and 0.8 ng/l. for dieldrin. Duplicate extraction and analyses of aliquots of selected samples and water mixtures spiked with known concentrations of pesticide suggest that the overall quantitative variability of the technique was about $\pm 25\%$ at the 1 ng/l. level. Usual minimum detectability limits were: DDT, 8.0 ng/l.; DDD, 0.8 ng/l.; DDE, 0.4 ng/l.; dieldrin, 0.4 ng/l.; aldrin, 0.2 ng/l.; and lindane, 0.1 ng/l. The data were corrected for the 60% extraction efficiency observed when water spiked with authentic pesticides (5 ng/l. DDE and dieldrin) was extracted.

Results and Discussion

There are numerous problems involved in the analysis of pesticide concentrations at these very low levels. For example, contamination from a variety of sources, including sample bottles, surface slicks, and laboratory glassware, is always a potential problem. In this instance, all glassware, sample bottles, and solvents were tested periodically, and the extracts checked for pesticide or PCB contamination. Only in the two cases cited previously were contaminating compounds found. Similarly, since there was no correlation of the concentration of pesticide in the samples with the wind or sea conditions prevailing at the time of sampling (hence surface slick conditions), lowering of sample bottles through the surface seems not to have been a source of contamination.

The concentrations of DDE and dieldrin in the ocean water samples are reported in Table I. Both DDE and dieldrin were detected in all but four samples. The mean concentration of DDE was 3.8 ng/l., whereas the corresponding dieldrin value was 5.8 ng/l. The concentrations of DDT and DDD were less than the detectability limits of this technique. Lindane and aldrin were also generally undetectable in these samples.

Peaks corresponding to the retention times of lindane and aldrin were observed in some samples. At station 20125 a trace (0.1 ng/l.) of lindane was present at the surface, at 50 m, and at 1000 m depth, and the surface aldrin concentration was 0.2 ng/l. Water from station 20127 contained 0.15 ng/l. lindane at the surface and 50 m and 0.6 ng/l. at a depth of 1000 m. Peaks corresponding to DDE and dieldrin (refer to Figure 2A) are clearly evident in the sample chromatogram in Figure 2B. Repeated extraction of aliquots of water from the same original sample produced very similar results qualitatively and quantitatively, whereas extraction of surface water samples from stations a short distance apart yielded values which are apparently unrelated (stations 20145-20147).

Perhaps the most striking features of the data is the lack of any systematic variation in concentration of pesticide with depth or distance from shore. In the latter respect, the data presented here are in agreement with the conclusions of two previous reports (5, 6), both of which reported that chlorinated hydrocarbon concentrations did not vary systematically with distance from shore in the North Atlantic. Indeed, a dominant feature of previous reports and the data presented here is the wide range of chlorinated hydrocarbon concentrations even in samples collected only a few miles apart. Apparently atmospheric transport, the postulated principal transport route of pesticides to the ocean, does not lead to entirely uniform oceanic distribution of those compounds (at least in the North Atlantic) as is assumed in most distribution system models (4, 8).

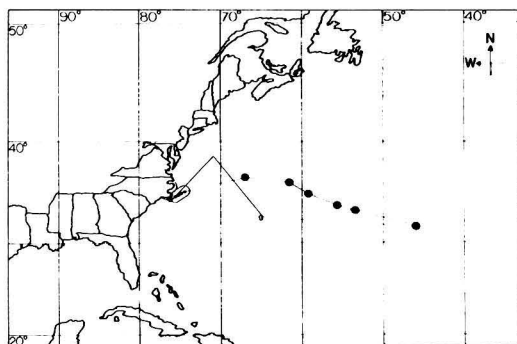


Figure 1. Chart of North Atlantic Ocean sample sites at which water was collected for pesticide analysis during cruise E-8B-72 of the R. V. Eastward

Station numbers (from east to west) are: 20120, 20125, 20127, 20129, 20132, 20139, 20144, 20145, 20146, and 20147

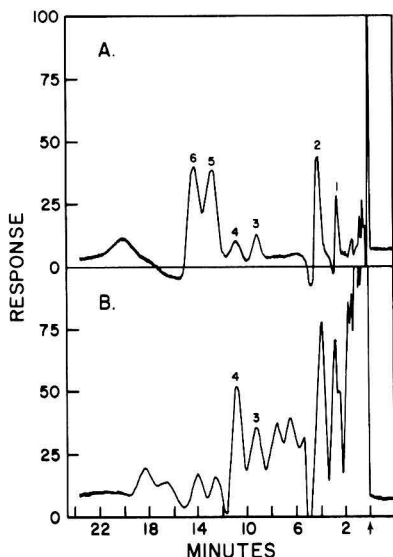


Figure 2. Chromatograms of chlorinated hydrocarbons
A. Mixture of six pesticides, 1-lindane, 2-aldrin, 3-DDE, 4-dieldrin, 5-DDD, and 6-DDT. B. Extract of ocean water from 1000 m depth at station 20129

Table I. Concentrations (ng/l.) of DDE^a and Dieldrin^b in North Atlantic Ocean Water of 0, 50, 500, and 1000 m Depth

| Depth, m | Mean ± SD | North | | | | | | | | | |
|----------|-----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| | | 34° 32' | 35° 02' | 35° 08' | 35° 13' | 37° 07' | 36° 17' | 35° 00' | 33° 50' | 33° 22' | 32° 00' |
| | | West | | | | | | | | | |
| Station | | | | | | | | | | | |
| | | 20147 | 20148 | 20145 | 20144 | 20139 | 20132 | 20129 | 20127 | 20125 | 20120 |
| DDE | | | | | | | | | | | |
| 0 | 4.9 ± 5.2 | 3.5 | 3.9 | 18.1 | 6.0 | 7.5 | 3.3 | <0.35 | 4.1 | 0.7 | 1.4 |
| 50 | 2.7 ± 3.6 | ... | ... | ... | 0.7 | 4.3 | 10.3 | <0.35 | 0.7 | 2.1 | 1.0 |
| 500 | 4.0 ± 5.3 | ... | ... | ... | 2.3 | 5.1 | 15.4 | 0.1 | 0.2 | 2.3 | 2.5 |
| 1000 | 3.0 ± 2.5 | ... | ... | ... | ... | 1.2 | 4.9 | 7.1 | 0.8 | 2.2 | 1.5 |
| Dieldrin | | | | | | | | | | | |
| 0 | 6.4 ± 5.6 | 6.2 | 19.4 | 2.4 | 6.1 | 0.4 | 10.6 | 6.1 | 3.9 | 0.5 | 8.7 |
| 50 | 6.2 ± 2.7 | ... | ... | ... | 5.7 | 6.4 | 3.3 | 8.1 | 9.8 | 2.2 | 7.8 |
| 500 | 3.6 ± 4.3 | ... | ... | ... | 6.2 | 4.8 | 11.9 | 0.4 | <0.4 | 1.1 | 1.0 |
| 1000 | 6.9 ± 6.2 | ... | ... | ... | ... | 8.1 | 4.0 | 18.3 | 6.3 | 4.8 | <0.4 |

^a Mean concentration of DDE = 3.8 ± 4.3. ^b Mean concentration of dieldrin = 5.8 ± 4.8 ng/l.

Additionally, the present data do not indicate that pesticide concentrations necessarily decrease with depth, at least to 1000 m. At least one previous study has reported a tendency of decreased concentrations with depth. Harvey et al. (5) observed a general decrease in PCB concentration from the surface to 200 m depth. However, that tendency was not universal in the samples analyzed. Indeed, the variation of surface PCB concentrations was much greater than the difference between surface and 200-m concentrations. Our data are in agreement with the more recent results of Harvey et al. (7) which suggest no systematic decrease of PCB concentration to a depth of 2000 m.

The data presented here indicate that the concentrations of both DDE and dieldrin are apparently unrelated to depth down to 1000 m. One hypothesis which might explain the observed variability (both with depth and distance from shore) is that pesticides adsorbed to particulate matter (planktonic organisms, organic aggregates, or even inorganic particulates) may be much more significant to the overall transport of these compounds in the sea than those dissolved in water. These particles may have concentrated the pesticides at their surfaces by adsorption or within their nonpolar constituents by dissolution. If a significant proportion of the pesticides were associated with sedimenting particulate material, then the concentrations at great depth could be more directly related to atmospheric or other inputs than if diffusive movements of dissolved materials dominate their transport within the sea. If this explanation is valid, then it might be expected that biological decomposition or autolysis of sinking organic particles could release pesticides to the water as the particles move toward the oxygen minimum layer. Density discontinuities in the water column might then be sites of greater pesticide accumulation. In the area of the Atlantic where these samples were collected, the permanent thermocline and the bottom of the oxygen minimum layer occur at about 1000 m depth. If this proposed mechanism of pesticide transport is valid, then lower pesticide concentrations might be observed in the waters from 1000 m to the bottom. However, studies of deep (below 1000 m) North Atlantic Ocean water samples indicate that other chlorinated hydrocarbons (PCB) have been transported to a depth greater than 5000 m (7).

The speculative conclusions of these and other authors concerning chlorinated hydrocarbons are based on data from

only a few samples and only from the North Atlantic. Without further reports from other ocean basins, generalization in this regard is exceedingly hazardous. Further, given possible introduction of consistent errors in this and other trace level chlorinated hydrocarbon studies, data reported should all be considered approximate. Intercomparison of values from various samples reported in any one study seems to be the most valid use of the data, whereas citation of absolute concentrations and comparisons with other reports are less well founded. Nevertheless, the average value of 3.8 ng/l. DDE agrees fairly well with the concentrations of 5–15 ng/l. arrived at by various models of DDT distribution (4, 8). However, most predictions suggest that this concentration should exist in the upper 100 m, which corresponds to the traditionally conceived mixed layer of the ocean. Additionally, the predictive models assume uniform distribution of the pesticides throughout that layer in all the world's oceans. Given a mixed layer (100 m depth) volume of 0.025×10^{24} ml (4) and a DDT concentration of 5.0 ng/l., the total DDT in the mixed layer would be 0.125×10^{12} grams. This amount is about 5% of all the DDT produced through 1972 (4). If, as our data indicate, DDT (as DDE) (3.8 ng/l.) is essentially mixed to a depth of 1000 m by some mechanism, then that layer could contain approximately 40% of the DDT produced through 1972.

It is inappropriate to conclude that the above calculations represent the actual situation in the various oceans, the western North Atlantic not being typical either in water movement patterns or exposure to pesticides. Certainly, the number of pesticide analyses thus far reported do not adequately delineate worldwide oceanic pesticide distributions. Additional water and sediment sample analyses from greater depths and various oceans will be necessary to determine whether, as has been inferred, the ocean is the ultimate site of accumulation of these toxic compounds.

Acknowledgment

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Lead and Cadmium in Dusts and Soils in a Small Urban Community

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■ In and around well-kept homes painted with low lead paints situated in a small urban community, large amounts of lead and cadmium are found. High trace metal amounts are also found at nonresidential sites. Much of the lead is probably of automotive origin. Lead levels in dusts within homes average 600 ppm and 680 $\mu\text{g}/\text{m}^2$. In nonresidential interiors, dusts average 1400 ppm Pb and 2040 $\mu\text{g}/\text{m}^2$. Unexpectedly high cadmium accumulations are found, especially in carpet dusts from rubber-backed carpets. High nonresidential settled dust and soil lead contents are due to higher traffic flows. The lead content of outdoor residential dust is 600-1950 ppm and 90-6640 $\mu\text{g}/\text{m}^2$. These values increase several times around nonresidential sites. Lead and cadmium from trace urban dusts are a significant addition to the child body burden.

Information is available on many aspects of environmental lead and cadmium levels (1, 2). Brief surveys have been made of urban dust and soil lead levels in particular. However, comprehensive surveys are lacking.

Kreuger (3, 4) found 1200 ppm lead in house dust samples in 27 samples taken in adjacent and far suburbs of Boston and Cambridge. Core city house dust samples averaged 2000 ppm. Core city gutter samples ranged in lead from 400 to 9000 ppm. Street dusts from residential and commercial sites averaged 1636 and 2413 ppm for 77 cities (1). Levels measured in these studies are much lower than those usually found in truly dilapidated homes—50 000-400 000 ppm lead (1). Surveys, generally in connection with edible crop studies, indicate lead levels for the top 15 cm of soil as high as 228 ppm in the vicinity of a high traffic density road (5, 6). As much as 10 000 ppm lead in the top 1 cm of soil has been reported (7).

Studies by Olson and Skogerboe (8) and Lamb (9) tend to confirm an automotive origin of lead in urban soils and dusts. In these studies, lead was found in major proportion in the iron-rich fraction of the dusts and soils. This is significant as airborne lead derived from auto exhaust is associated with iron.

However, contradictory evidence concerning dust and soil lead sources has recently been offered by Ter Haar and Aroonow (10). They found similar lead levels in rural and urban yards at corresponding distances from painted frame houses. The authors conclude, "... nearly all the lead in dirt around the house is due to paint from the house . . ." Levels of lead for the urban study were highest near the house (2000 ppm). However, the urban lead levels measured at other locations were lower than in other studies, averaging only 600 ppm at the curb and 1100 ppm in the gutter.

Cadmium levels and toxicity were reviewed by Fleischer et al. (2). Even less data are available on urban cadmium dust and soil levels than on lead.

This report presents the results of an area-wide survey of lead (and cadmium to a lesser extent) in settled dusts and soils in a small urban community, Champaign-Urbana, Ill. (population 100 000). Approximately 1400 samples, both indoor and outdoor, were taken in residential and nonresidential areas. It was desired to measure these trace metals, which offer a risk to children, in a "best world" situation rather than in decaying neighborhoods. The homes selected were in good repair, painted with nonlead or low lead paints, and were located in relatively low traffic density areas. Measurements were also made in nonresidential areas such as schools, streets, and offices. Although airborne lead levels as high as 3.8 $\mu\text{g}/\text{m}^3$ were measured in the nonresidential areas of Champaign-Urbana, these levels are low in comparison to major cities.

Experimental

Sampling. A vacuuming technique with a special nylon filter holder was used to gather settled dusts. The filter holder is shown in Figure 1. A glass fiber paper (Gelman Type A) insert was used in each sampling run. A portable pump (Millipore Corp., Bedford, Mass., Model XX61-000-00) was the vacuum source. The vacuumed dust was trapped in the upper chamber of the nylon holder. The used filter and the dust gathered were placed in tared glassene envelopes. Glassene envelopes and clean filters were humidity and temperature equilibrated for 24 h before initial and final weighings. When weighings were made or dusts handled, plastic gloves were worn since bare hands could contaminate the samples.

A 0.5 × 0.5 m wood template was placed on the surface to be sampled, allowing results to be reported on an area basis ($\mu\text{g}/\text{m}^2$) as well as on a weight basis ($\mu\text{g}/\text{Pb}/\text{g}$ dust or ppm). The method of dust sampling is shown in Figure 2. Indoor samples were always taken in the central area of a room, away from the walls.

One pass with the special vacuum holder was made of the 0.25 m² area in taking each dust sample. To test the efficiency of the sampling technique, two passes on a given area were made in 41 cases. The results indicate 90% of the lead is picked up in the first sweep. The error in the weight fraction of lead due to carrying out only one sweep was less than 6%.

Soil samples were taken with a standard soil borer (Oakfield soil sampler, Model B, Oakfield Apparatus Co., Oakfield, Wis.). A 15-cm soil core was removed with the Oakfield auger, but only the top 2.5 cm was used in this study.

Analytical. Dust samples were screened on a 30-mesh (ASTM) stainless steel screen before analysis. Soil samples were dried for 4 h at 105 °C after screening on a 2-mm (10-mesh ASTM) stainless steel standard sieve. If the collected sample weighed less than 6 g, then the entire sample was used in the analysis. A 3–6 g subsample was obtained from dust samples weighing more than 6 g by use of a 5 × 5 cm riffle.

Dust samples were digested with 8 N HNO₃ for 4 h at 85 °C. Deionized water was added up to a reference volume, and the solution was vacuum filtered through No. 1 Whatman paper into precleaned polypropylene vials. Soil samples were digested for 4 h at 180 °C and were treated in a similar manner to the dusts.

Analytical determination of lead and cadmium is by atomic absorption spectrometry using a Jarrell-Ash Model 810. Lead absorption was measured at 283.3 nm with background correction at 287.2 nm. Cadmium absorption was measured at 228.8 nm with background correction at 226.5 nm. The detection limits are 0.02 ppm lead and 0.005 ppm cadmium in the analytical solution. For a 1-g sample the detection limits are 0.2 ppm Pb and 0.05 ppm Cd. For a 100-mg sample the detection limits are 2.0 ppm Pb and 0.5 ppm Cd. The relative standard deviation at the detection limit is approximately 50%. Over the normal working range, the relative standard deviation is approximately 5%. Complete detailed sampling and analysis procedures are given in Solomon et al. (11).

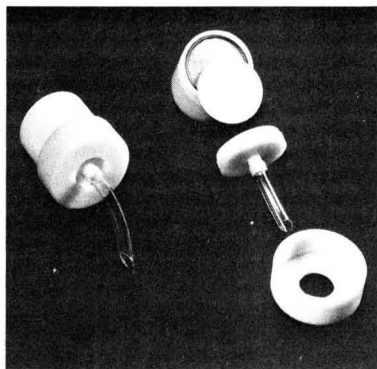


Figure 1. Dust sampler

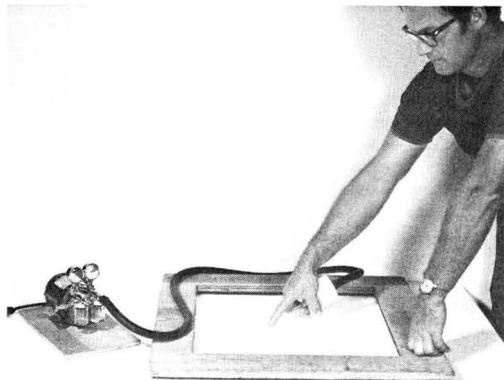


Figure 2. Dust sampling procedure

Of the 1400 samples taken, 115 soil and 81 dust samples were taken in replicate, i.e., a pair of samples was taken at the same time and site, 1 m apart. Analysis of the data using the *t*-test indicated no significant difference of the pair means either on a weight or area basis at a 95% confidence level. Confidence level on the data is ±20% including analytical and sampling factors.

Results and Discussion

Interior Residential Measurements. A total of 239 floor dust samples were taken in 12 homes. Four of the homes were sampled twice. Ten of the homes were single-family residences, and two were located in multistory apartment buildings (Sites F and K). A summary of the indoor residential lead and cadmium data is shown in Table I. For the 12 homes, average indoor lead levels of 600 ppm and 680 μg/m² were found. All of the homes were upper middle class abodes in extremely fine condition as regards to paint chipping, peeling, etc. Furthermore, all samples were taken in the central room area away from the walls. It would seem that a substantial fraction of the very high lead levels must be due to lead settling from automobile emissions. Cadmium levels were also quite high as will be discussed below.

Typical results for individual homes have been tabulated for rug-covered surfaces and nonrug-covered surfaces in Table II. The lead content of dust found on nonrug-covered surfaces (wood or tile) is generally higher than that found on rugs, 950 ppm lead vs. 450 ppm lead on the average. However, the total amount of settled lead (as measured on an area basis) is higher on rugs, i.e., there is more dust accumulation on rugs than on bare floors.

Cadmium contents as high as 105 ppm and 219 μg/m² were measured in some homes. On rugs, large amounts of cadmium are found—44 μg/m² on the average. This is probably due to the rubber backing found on many carpets. A sample of this material assayed 3000 ppm cadmium. Abrasion would cause the cadmium presence in dust.

Ventilation patterns, number of pets, and number of inhabitants as well as airborne lead levels can be expected to influence the dust lead levels. Outdoor air lead levels were measured (12) over a long period of time at eight of the 12 sites (A, B, C, D, E, G, I, L) and fairly close to four others (F, H, J, K).

These 10 single-family residences all had forced air natural gas heating systems except for site L. Although indoor airborne lead levels would be 30–60% less than outdoor levels in

Table I. Mean Lead and Cadmium Levels in Settled Floor Dusts, Residential Sites

| Code | Lead | | Cadmium | |
|-------------|------|-------------------|---------|-------------------|
| | ppm | μg/m ² | ppm | μg/m ² |
| A | 1440 | 1180 | 28 | 26 |
| B | 690 | 710 | 19 | 14 |
| C | 940 | 1700 | 10 | 31 |
| D | 760 | 580 | 10 | 11 |
| E | 900 | 1590 | 20 | 37 |
| F | 350 | 760 | 48 | 132 |
| G | 240 | 100 | 26 | 7 |
| H | 500 | 70 | 25 | 3 |
| I | 170 | 120 | 7 | 4 |
| J | 270 | 400 | 9 | 15 |
| K | 430 | 650 | 12 | 15 |
| L | 460 | 220 | 12 | 6 |
| Av 12 sites | 600 | 680 | 18 | 25 |

the fall and winter months corresponding to the period during which the indoor dust samples were taken, it is not unreasonable to expect airborne indoor trends to follow the outdoor trends (13, 14).

Although outdoor airborne lead levels were low, with a mean of $0.28 \mu\text{g}/\text{m}^3$ and range ($0.18\text{--}0.34 \mu\text{g}/\text{m}^3$), sites with the highest outdoor airborne lead had the highest settled dust lead levels. An exception is site H, which would be expected to have somewhat higher lead dust levels than measured.

Settled dust lead levels at sites F and K, the apartment residences, are somewhat lower than might be expected from traffic levels in the vicinity. However, outdoor air lead levels were not measured, and little is known about indoor airborne lead levels in apartment buildings. The magnitude of the lead dust levels is similar to that found by Kreuger (4) in suburban dust near Boston.

Interior Nonresidential Measurements. For a more complete picture of human exposure, it is desirable to know the level of lead and cadmium in dust in locations where

people work, visit, and shop outside of the home. Presumably, adults, on their clothes and shoes, inadvertently carry dust found in these areas back into the home where it becomes available for infant/child ingestion.

Over 350 samples were taken in university laboratories and classrooms, schools, hospitals, food markets, etc. Samples were taken in the central floor area away from the walls. Partial results are shown in Table III. Lead levels in corridor dust are about as high as in interior rooms. Extremely large amounts of lead and cadmium are found everywhere, ranging from 500 to 3000 ppm lead and 1–50 ppm cadmium. As in residences, high total cadmium levels are associated with rubber mats or rubber-backed carpeting.

Astonishingly high levels of lead and cadmium are found in chemical laboratories. Paint chipping was not observed in any of the laboratories (or indeed in any of the other locations sampled). Since lead (and cadmium) levels in offices adjacent to the laboratories are much lower, some of the trace metals in the laboratory dust are probably of local chemical origin.

Average levels of lead and cadmium for the nonresidential survey are shown in Table IV. Chemical laboratories are excluded from the data averaged in this table. The average lead values of 1400 ppm and $2040 \mu\text{g}/\text{m}^2$ would be nearly doubled if the laboratories were included.

Levels of lead and cadmium are nearly twice residential averages. In the case of lead, this reflects the magnitude of outdoor airborne lead levels in the nonresidential areas, 2–5 times residential averages (12).

Outdoor Residential Measurements. Outdoor lead and cadmium were measured in the soils and dusts surrounding the 10 one-family residences of the indoor study. Eight of the homes were painted frame houses (paint assay <1% lead), whereas the other two had small amounts of painted trim (paint assay 5% lead). Cadmium assays of the paint indicated nine <50 ppm and one of 150 ppm. All were in low traffic density areas, and all were in outstanding condition with no evidence of paint peeling or chipping.

All of the 288 soil and dust samples taken were analyzed for lead, and 177 were analyzed for cadmium. The data have been grouped by areas around a typical house in a composite (Figure 3). Because all homes are not oriented similarly, and groupings cover differing distances from the road and house, some of the data groups are slightly skewed. Medians and range of data are shown. Near is defined as ≤ 1 m.

Lead levels in dusts are very high both near the road and near the house. The range in dust lead content is 240–6640 ppm away from and 130–11 760 ppm near to the house. Soil lead levels are somewhat higher both near the road and house, but there is not a great deal of variation in soil lead concentrations. Soil lead values fall in the range 20–1060 ppm.

Presumably, high lead in soils and dusts adjacent to roadways would be due to auto emissions or re-entrainment of settled dusts. High lead levels adjacent to the house would be due to both paint weathering as well as leaching and washoff of settled airborne automotive lead on roof and window sills. Lead levels are high everywhere in the vicinity of the home. It is not simply a question of high levels only immediately adjacent to the exterior of the house. It seems unreasonable, therefore, to ascribe all the lead and all the danger to paint (10).

For clarity, total amounts of lead on an area basis have not been shown in Figure 3. The net amount of lead found in the home areas was surprisingly large. The net amount of lead was largest in gutters with a median value of $21\ 300 \mu\text{g}/\text{m}^2$ and a range of $1270\text{--}211\ 000 \mu\text{g}/\text{m}^2$. In driveways the median value was $5820 \mu\text{g}/\text{m}^2$ with a range of $1050\text{--}86\ 000 \mu\text{g}/\text{m}^2$. On walks the median was $1590 \mu\text{g}/\text{m}^2$ with a range of $720\text{--}15\ 200 \mu\text{g}/\text{m}^2$. On surfaces adjacent to the house, the median lead content of dust was $1840 \mu\text{g}/\text{m}^2$ with a range of $200\text{--}9100 \mu\text{g}/\text{m}^2$.

Table II. Typical Lead and Cadmium Levels in Settled Floor Dusts, Residential Sites

| Site | No. of samples | Lead | | Cadmium | |
|---------|----------------|------|--------------------------|---------|--------------------------|
| | | ppm | $\mu\text{g}/\text{m}^2$ | ppm | $\mu\text{g}/\text{m}^2$ |
| A Rugs | 7 | 830 | 1490 | 24 | 43 |
| Nonrugs | 13 | 1780 | 1020 | 29 | 17 |
| B Rugs | 5 | 420 | 460 | 17 | 20 |
| Nonrugs | 10 | 480 | 140 | 25 | 6 |
| F Rugs | 6 | 240 | 350 | 66 | 71 |
| Nonrugs | 1 | 290 | 60 | 105 | 22 |
| G Rugs | 11 | 220 | 110 | 14 | 7 |
| Nonrugs | 3 | 320 | 70 | 71 | 8 |

Table III. Typical Lead and Cadmium Levels in Settled Floor Dusts, Nonresidential Sites

| Site | No. of samples | Lead | | Cadmium | |
|------------------------------|----------------|--------|--------------------------|---------|--------------------------|
| | | ppm | $\mu\text{g}/\text{m}^2$ | ppm | $\mu\text{g}/\text{m}^2$ |
| Offices, hallways | 36 | 3380 | 3010 | 9 | 8 |
| Offices, nonrugs | 11 | 1450 | 640 | 13 | 7 |
| Classrooms, nonrugs | 8 | 930 | 160 | 1 | 0 |
| Offices, rugs | 6 | 2320 | 11 780 | 1033 | 2443 |
| Offices, nonrugs | 1 | 2960 | 560 | 1060 | 200 |
| Public school, rugs/mats | 10 | 730 | 3990 | 29 | 122 |
| Public school, nonrugs | 17 | 650 | 200 | 7 | 4 |
| Public school, rugs/mats | 12 | 410 | 2360 | 30 | 115 |
| Public school, nonrugs | 26 | 430 | 210 | 19 | 5 |
| Hospitals, entry areas, rugs | 11 | 620 | 7940 | 20 | 390 |
| Hospitals, corridors, rooms | 11 | 360 | 180 | 22 | 4 |
| Supermarkets | 34 | 490 | 100 | 9 | 2 |
| Chemical laboratories | 35 | 11 400 | 3390 | 185 | 57 |

Table IV. Mean Lead and Cadmium Levels in Settled Floor Dusts, Nonresidential Sites

| | No. of samples | Lead | | Cadmium | |
|--------------|----------------|------|--------------------------|---------|--------------------------|
| | | ppm | $\mu\text{g}/\text{m}^2$ | ppm | $\mu\text{g}/\text{m}^2$ |
| Rugs/mats | 42 | 860 | 6670 | 70 | 604 |
| Nonrugs/mats | 212 | 1500 | 1120 | 19 | 12 |
| All floors | 254 | 1400 | 2040 | 44 | 110 |

Cadmium levels, by weight, were somewhat higher in soils and dusts near the house (1 ppm in soils, 6–8 ppm in dusts). Total cadmium dust levels were relatively uniform everywhere: 7–20 $\mu\text{g}/\text{m}^2$.

The 10 homes taking part in the above study are an ideal situation: relatively low traffic in the vicinity, low or nonleaded paints used, and good maintenance. If homes that do not meet these conditions are studied, then soil lead levels are found to increase dramatically.

A special study was made of seven additional frame houses. Each was painted with an identical type of high leaded paint (27% Pb by weight). The houses were located in higher traffic density areas (airborne lead 2–3 times higher than in the residential). Soil lead levels are shown in Figure 4 as the curve

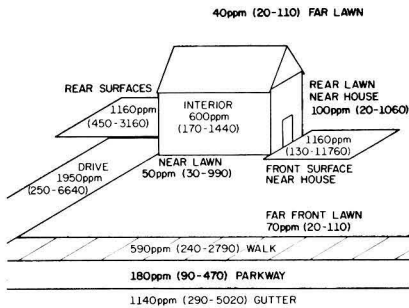


Figure 3. Composite lead in dust and soils in residential areas, median and range

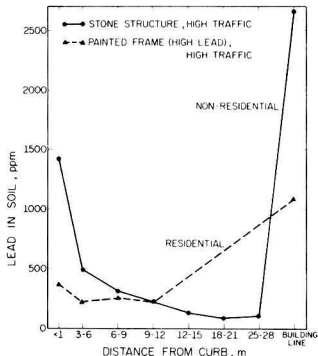


Figure 4. Mean lead in soils in high traffic density sites—residential and nonresidential

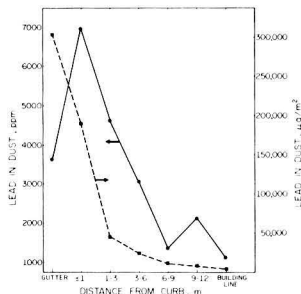


Figure 5. Mean lead in dust—nonresidential sites

labeled residential. However, the houses are not presently used as personal residences, although they were so used in the past.

Soil lead levels are much higher in the vicinity of these seven houses as compared to the 10 residences previously studied. The largest increases are in the very high soil lead found adjacent to the curb and adjacent to the house. However, these maximum soil lead values are of the same order of magnitude as the lead content of the settled dusts found in the walks and driveways of the 10 houses painted with low lead paints (see Figure 3). Thus, lead paint use is not the sole indicator of high settled lead concentrations.

Outdoor Nonresidential Measurements. A survey of lead and cadmium in outdoor dusts and soils was made in many of the same nonresidential locations used in the indoor survey. All buildings were of stone or brick construction. Dusts were sampled at seven sites (195 samples) and soil at 20 sites (183 samples). All samples were analyzed for lead and 70% for cadmium. The lead content of settled dusts as a function of distance from a road is shown in Figure 5.

In Figure 5 both the lead content of the dusts by weight and the total lead accumulation fall off with distance from the road. The roads in question all had traffic flows in the range of 5000–20 000 cars/day. Mean accumulations as high as 190 000 $\mu\text{g}/\text{m}^2$ were measured on the sidewalk. Dust lead contents were about twice that in residential areas. No lead increase adjacent to the buildings was noted in the dust measurements. However, at only two sites could one take undisturbed dust samples near the building line.

The mean soil lead transect for these stone and brick buildings is shown in Figure 4. Soil lead is high near the road and falls off but then increases to the highest level adjacent to the stone buildings. The latter increase is possibly due to leaching of window trim paint, but more likely is due to wash-off of nonpaint source settled lead from roofs or ledges.

Soil lead contents are several times higher than normal residential values due to higher vehicular traffic in the area. Curb soil values are also higher than those found in the special study of the seven homes painted with high lead paint also shown in Figure 4. Again, this is due to the even higher traffic levels in the nonresidential case.

However, the soil lead content near the stone and brick building lines is higher than that found adjacent to the frame houses painted with high lead paint. This strongly suggests that a wash-off of settled lead of airborne origin occurs.

Cadmium levels average 1 ppm in soils and 2–6 ppm in dusts. No trends are discernible. Total cadmium in dust falls from 134 to 1 $\mu\text{g}/\text{m}^2$ near the building line.

Potential Consequences. Implications of the high levels of lead and cadmium found in the environment are quite serious for the young child or infant. A child might be expected to have 10 mg of dust on its fingers (15). If the child spent most of its time indoors and placed its fingers in its mouth 10 times, an average of 60 μg of lead and 2 μg cadmium per day might be ingested. If appreciable time were spent outdoors or in a nonresidential setting, these values could be doubled or tripled. Since the maximum permissible daily intake has been estimated at 70–500 $\mu\text{g}/\text{day}$ (15), these ingestion values represent significant amounts of lead and could represent a danger to children previously thought to be at no risk from paint-induced lead poisoning.

The permissible daily cadmium intake is not known, and scant information is available concerning subclinical cadmium toxicity (2). The estimated cadmium intake for adult non-smokers is 20–50 $\mu\text{g}/\text{day}$, almost totally from food (2). Children might be expected to take in approximately one-half the adult food level (16). Therefore, cadmium ingestion from dusts

could be a significant fraction of their daily intake and might represent an added risk.

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Infrared Spectra of Petroleum Weathered Naturally and Under Simulated Conditions

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■ The feasibility of weathering petroleum in confined areas and under simulated conditions was explored. Four separate weathering systems were studied with as many as 60 different oils. Infrared spectra of oils weathered in these different systems were compared with each other and with unweathered oils using a computer ratio method. The results on an oil from an actual spill case showed that oils weathered in three of these systems to the same extent as oil taken from the spill.

The infrared spectrum of an organic chemical can be used for identification by matching the "fingerprint" with that of a known sample. The spectrum of petroleum can be treated like that of a pure compound, and its "fingerprint" can be matched to that of a sample of known origin (1-8). This technique has obvious applications in determining the source of oil spills (2, 6, 8). However, petroleum is a composite of hundreds or even thousands of organic chemicals rather than a pure compound. Some of these components are soluble in water, have high vapor pressures, and are susceptible to photo-oxidation or other means of degradation. For this reason, we have been investigating the effects of weathering on all types of petroleum.

Since it is not always easy to obtain samples of actual oil spills, we have tried weathering petroleum in confined areas under natural and simulated conditions. Herein, we discuss the weathering systems and demonstrate their capability to simulate actual conditions by comparing the results on an oil taken from an actual spill with those obtained by weathering the same oil in confined areas.

Experimental

Measurement of Spectra. Water was removed from weathered oils by centrifuging at 35-40° for 0.5-2.0 h, removing the bulk water with a syringe, adding anhydrous MgSO₄, and centrifuging at 35-40 °C for another 0.5-2.0 h (9). Spectra were measured on a Perkin-Elmer Model 521 spectrometer using demountable AgCl cells with 0.05 or 0.075-mm spacers.

Weathering Grids. During the past year we have explored the applicability of four weathering systems:

i) *Narragansett Bay Weathering Grid.* This grid consists of ten 55-gal drums floating in truck inner tubes and attached to a floating dock about 40 ft from shore in 12 ft of water (Figure 1). Each drum is fiberglassed on the inside to eliminate reactions between the oil and the container. In addition, each drum has four 8-in. slits and a series of twenty 1-in. holes cut in an X-shape on the bottom to allow for the exchange of water.

ii) *On-shore Grid.* About 100 ft from Narragansett Bay, we have a grid of 10 all-fiberglass containers 18 × 18 × 18 in. (Figure 2). Seawater is continuously supplied to these containers at the rate of 1 gal/min from an aquarium pumping system; the water is taken directly from the Bay and is free of additional pollutants. Each container has an overflow pipe which regulates the water level at 3 in. from the top.

iii) *Laboratory Grid.* This grid is identical to the one in ii, except that a continuous flow system is not used since our laboratory is located 6 mi from the Bay. However, the seawater is replaced at the beginning of each experiment. Artificial illumination for these weathering experiments is provided by

four sunlamps located 4 ft above the weathering grid. The water in each container can be cooled by passing tap water through a copper coil. Agitation is provided by an Al paddle hinged to the side of each container and attached to a windshield wiper motor by a nylon line. In some experiments, agitation was provided by "bubbling" air through the water; the aeration increased the rate of evaporation and oxidation.

iv) Laboratory Roof Grid. This grid, which is identical to *iii*, is located on the roof of our laboratory to take advantage of natural sunlight.

Discussion

Computer Method of Analysis. Previously, we have shown that the fingerprint of an unknown oil can be matched to that of its source oil by a computer searching technique (1). The computer method is described in Table I. Infrared spectra of oils from known origins and of the unknown oil are measured, % transmissions of 18 selected bands in the 650–1200 cm^{-1} region and of the background (I_o) at 650 cm^{-1} are recorded, and these are converted to absorptivities (steps 1 and 2). The ratios of absorptivities of each known to those of the unknown are calculated (step 3), and the correct match is identified by the known/unknown having the most ratios closest to the average.

One very important feature of this method is that sample pathlengths of both the known and unknown are eliminated in step 5a. This is not essential if the sample pathlength is known exactly, but this is the case only when fixed pathlength cells are used.

To determine the infrared bands that are sensitive to weathering and those that are stable, we treat the unweathered oil as an unknown in the computer analysis and compare it to all of its weathered samples. Thus, we have to visually scan the numerical computer output for 18 bands of nine weathered samples of over 60 different oils. Recently, we

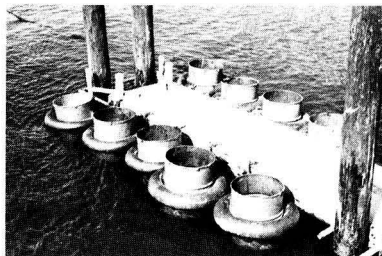


Figure 1. Floating weathering grid in Narragansett Bay located 40 ft from shore in 12 ft of water

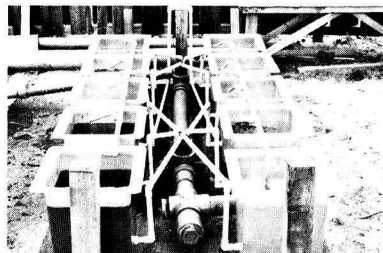


Figure 2. On-shore weathering grid showing system for circulating seawater through containers

found that the best way to correlate this large amount of data is to plot the differences between the "normalized" ratios and the ideal average, 1.0 (step 5b). By overlaying these plots for oils weathered at various lengths of time, the rate of change of each band can be determined.

Table I. Original Computer Searching Method^a

- 1) Absorptivities of known calculated and stored in computer file

$$a_i = \frac{A_i}{b} = \frac{1}{b} \log \frac{I_o}{I_i}$$

- 2) Absorptivities of unknown calculated

$$a_i'' = \frac{A_i''}{b''} = \frac{1}{b''} \log \frac{I_o''}{I_i''}$$

- 3) Ratios of absorptivities of each known to unknown calculated at each frequency

$$\frac{a_i}{a_i''} = \frac{A_i b''}{A_i'' b} = \frac{A_i}{A_i''} B$$

- 4) Average ratio for each known to unknown calculated

$$\frac{1}{N} \sum_{i=1}^N (A_i/A_i'') B = \frac{B}{N} \sum_{i=1}^N (A_i/A_i'') = BZ$$

- 5a) Ratios divided by average to make average 1.0

$$\frac{A_i}{A_i''} B/BZ = \frac{A_i}{A_i'' Z}$$

- 5b) Difference between ratios and 1.0 (average) calculated

$$\frac{A_i}{A_i'' Z} - 1.0 = \text{Diff}_i$$

- 6) Listing of number of bands for each known with difference (ratios-average) less than ± 0.05 , ± 0.10 , ± 0.25 , and ± 0.05

^a Definition of terms: a_i = absorptivity of i th band, A_i = absorbance of i th band, b = pathlength of cell, I_o = % transmission of background, I_i = % transmission of i th band, '' = values for unknown

sample, $B = b''/b$, N = total number of ratios, and $Z = \frac{1}{N} \sum_{i=1}^N (A_i/A_i'')$.

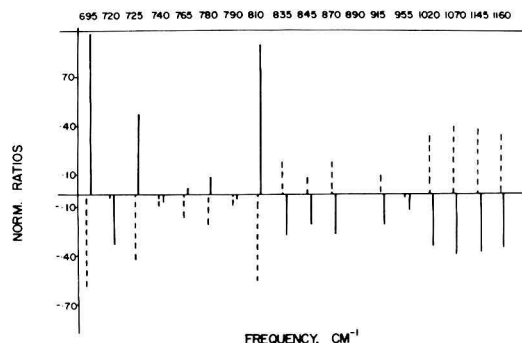


Figure 3. Bar-graph of "normalized" ratios minus ideal ratio of 1.0 using original method (step 5b in Table I) for weathered/unweathered - - - and unweathered/weathered —

The plotting can be done by a computer, and an example of the resulting bar-graph for the ratio of a crude oil to the same oil weathered for 2 weeks is shown in Figure 3 (solid vertical line). Ideally, the reverse comparison, i.e., weathered to unweathered, should give differences that are equal in magnitude but opposite in sign. However, as can be seen in Figure 3 (dashed vertical lines), this is not the case. The reason for this difficulty is obvious. For example, if the known/unknown ratio of absorptivities for a certain band is 2.0, then the reciprocal ratio (unknown/known) would be 0.50. Since these numbers are compared to the ideal average of 1.0, the latter value would be closer to the average. When listing the number of ratios within the limits (step 6), the latter ratio would be counted, whereas the former ratio would not be counted. In essence, by using the method described in Table I, comparison of a weathered/unweathered would not be exactly the same as the reverse comparison (unweathered/weathered). To

Table II. Revised Computer Searching Method^a

- 1) Absorptivities of known calculated

$$a_i = \frac{A_i}{b} = \frac{1}{b} \log \frac{I_0}{I_i}$$

- 2) Absorptivities of unknown calculated

$$a_i'' = \frac{A_i''}{b''} = \frac{1}{b''} \log \frac{I_0''}{I_i''}$$

- 3a) Ratio of absorptivities of each known to unknown calculated at each frequency

$$\frac{a_i}{a_i''} = \frac{A_i b''}{A_i'' b} = \frac{A_i}{A_i''} B$$

- 3b) Log of each ratio calculated

$$\log \frac{A_i B}{A_i''} = \log \frac{A_i}{A_i''} + \log B$$

- 4) Average log-ratio calculated

$$\frac{1}{N} \sum_{i=1}^N \left(\log \frac{A_i}{A_i''} + \log B \right) = \frac{1}{N} \sum_{i=1}^N \log \frac{A_i}{A_i''} + \log B$$

- 5) Average log-ratio subtracted from raw ratios to make average 0.0

$$\log \frac{A_i}{A_i''} + \log B - \frac{1}{N} \sum_{i=1}^N \log \frac{A_i}{A_i''} - \log B = \text{Diff}_i$$

- 6) Listing of number of bands for each known within limits of +0.025, +0.04, +0.10, and +0.15

^a See Table I for definition of terms.

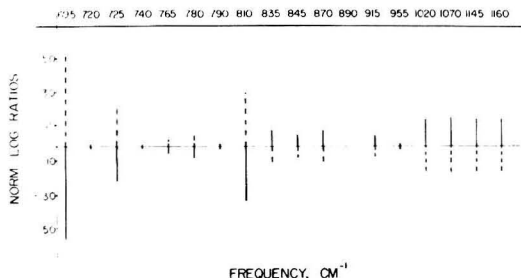


Figure 4. Bar-graph of "normalized" log-ratios obtained using modified method (step 5 of Table II) for unweathered/weathered - - - and for weathered/unweathered — (for same samples used in Figure 7)

correlate all of the spectral data on weathered and unweathered samples, it is essential that the comparisons be identical.

We have solved this problem by going to the log system described in Table II. Steps 1–3a are identical to those in the original method. However, in step 3b the log of the ratio is calculated, then an average log-ratio is calculated for each known/unknown, and this is subtracted from the raw log-ratios to give a new average log-ratio of 0.0. Thus, the differences are expressed as deviations from 0.0, and a weathered/unweathered ratio will be identical, except for the sign, to the reciprocal ratio. The ratios and reciprocal ratios of a weathered/unweathered crude oil are plotted by the log method in Figure 4; the ratios and reciprocal ratios are identical in magnitude.

The elimination of the sample pathlength of both known and unknown is preserved in the new method (step 5). Furthermore, the limits used in step 6, i.e., 0.025, 0.05, 0.10, and

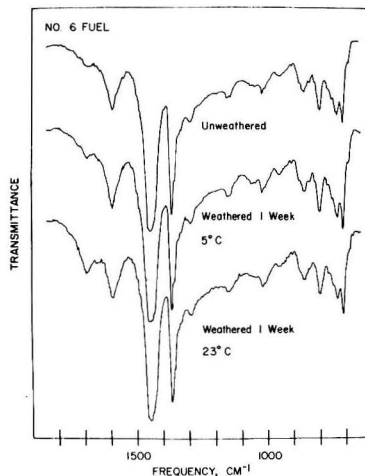


Figure 5. Infrared spectra of No. 6 fuel oil: unweathered, weathered 1 week at 5 °C, and weathered 1 week at 23 °C

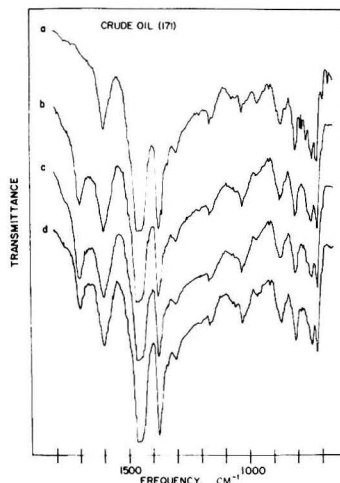


Figure 6. Infrared spectra of crude oil: a, unweathered; b, weathered in Bay grid for 2 weeks; c, weathered in roof grid for 2 weeks; d, weathered in laboratory grid for 2 weeks

0.15, correspond to 5, 10, 25, and 50% limits used in the original method.

Infrared Spectra of Petroleum Weathered in Confined Areas. Initially, the same oils were weathered in grids *i*, *iii*, and *iv* for two-week periods. Of the 10 containers in each grid, eight were used to weather oils that had not been previously weathered, the ninth was used to weather the same No. 6 fuel oil during each weathering cycle, and the tenth container was used as a control. Oil was not placed in the control container; however, the surface water was sampled, organics were extracted with CHCl_3 , and spectra measured after removing the solvent to test for the presence of petroleum. Petroleum was not detected in the control container during any of the experiments.

Since the weathering experiments were performed over a 1-yr period, the results on the No. 6 fuel oil that was weathered during each cycle gave a good indication of temperature effects. Infrared spectra of the No. 6 fuel weathered for 1 week at two extremes in temperature, i.e., 5 and 23 °C, are compared to the unweathered oil in Figure 5. The spectrum of the oil at the lower temperature was very similar to the unweathered oil, whereas at the higher temperature the carbonyl band at $\sim 1700\text{ cm}^{-1}$ increased significantly and sharp, weak bands in the fingerprint region of $700\text{--}1200\text{ cm}^{-1}$ started to disappear. We have found similar effects of temperature for all of the oils we have studied, i.e., that high temperatures cause "weathering" to proceed faster.

During each weathering cycle, different types of oils were weathered, e.g., heavy and light crudes; No. 2, 4, 5, and 6 fuels; and lubricating oils. We have weathered over 60 oils in these grids, and samples were collected and analyzed at 2, 7, and 14 days.

Typical spectra of three different types of oils weathered in the three grids are compared to the original unweathered oil in Figures 6–8. In each figure *a* is the unweathered oil, *b* the oil weathered in grid *i*, *c* weathered in grid *iv*, and *d* weathered in grid *iii*. The weathered samples of the crude oil (shown in Figure 6) were all collected after 2 weeks. There are differences between the spectra of the three weathered samples, since the rate of weathering was not identical in the three systems. Generally, the oils in the roof grid weathered faster than those in the Bay grid, whereas those in the laboratory grid weathered

slower. Using the computer ratio method of comparison, we found that ratioing the spectrum of the 1-week Bay sample to that of either the 2-day roof sample or the 2-week laboratory sample produced 18/18 ratios within 10% of the average. This is further demonstrated in Figure 7, where the spectrum for a 1-week Bay sample of No. 6 fuel is compared to that of a 2-day roof sample and a 2-week laboratory sample. In this case, the computer comparison of these spectra gave 17/18 ratios within 10% of the average when the Bay sample was compared to either the roof or the laboratory sample.

Visual comparison of the spectra of the weathered oils with those of the unweathered oils in the fingerprint region of $650\text{--}1200\text{ cm}^{-1}$ shows that the bands between 770 and 800 cm^{-1} have almost disappeared in the spectra of the weathered crude oil. These bands are undoubtedly due to light compo-

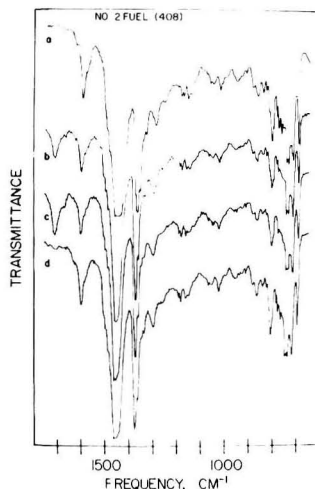


Figure 8. Infrared spectra of No. 2 fuel oil: a, unweathered; b, weathered in Bay grid for 2 days; c, weathered in roof grid for 2 days; d, weathered in laboratory grid for 2 days

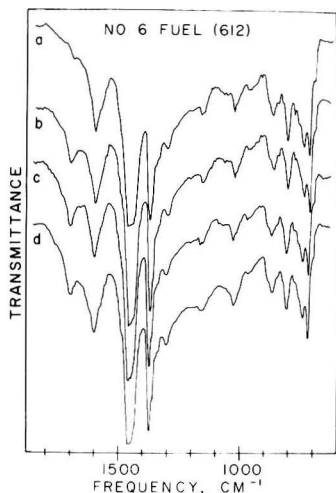


Figure 7. Infrared spectra of No. 6 fuel oil: a, unweathered; b, weathered in Bay grid for 1 week; c, weathered in roof grid for 2 days; d, weathered in laboratory grid for 2 weeks

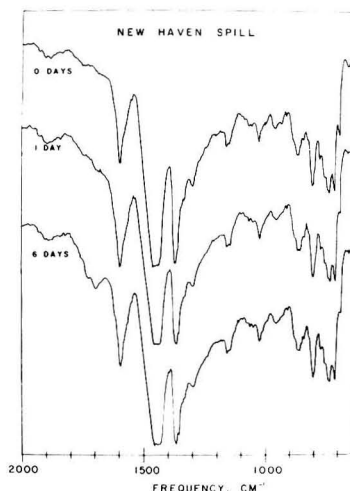


Figure 9. Infrared spectra of oil from New Haven spill; unweathered oil, weathered 1 day, and weathered 6 days

Table III. Comparison of Original and Weathered Oils from New Haven Spill

| | No. of bands within 10% (0.04) — 18 bands used in analysis | | | | | | | | | | |
|-------------------|--|------------------|-------------------|------------------|-------------------|---------------|----------------|-----------------|-----------------|------------------|-------------------|
| | Original | New Haven, 1 day | New Haven, 6 days | Narr. Bay, 1 day | Narr. Bay, 6 days | In-lab, 1 day | In-lab, 7 days | In-lab, 14 days | Aquarium, 1 day | Aquarium, 7 days | Aquarium, 14 days |
| Original | ... | 14 | 13 | 13 | 12 | 18 | 15 | 12 | 18 | 12 | 8 |
| New Haven, 1 day | ... | ... | 18 | 17 | 17 | 16 | 17 | 17 | 14 | 16 | 13 |
| New Haven, 6 days | ... | ... | ... | 16 | 18 | 14 | 16 | 16 | 14 | 16 | 16 |
| Narr. Bay, 1 day | ... | ... | ... | ... | 18 | 17 | 18 | 18 | 16 | 17 | 16 |
| Narr. Bay, 6 days | ... | ... | ... | ... | ... | 15 | 17 | 17 | 13 | 16 | 18 |
| In-lab, 1 day | ... | ... | ... | ... | ... | ... | 17 | 16 | 18 | 16 | 12 |
| In-lab, 7 days | ... | ... | ... | ... | ... | ... | ... | 18 | 15 | 18 | 16 |
| In-lab, 14 days | ... | ... | ... | ... | ... | ... | ... | ... | 13 | 17 | 18 |
| Aquarium, 1 day | ... | ... | ... | ... | ... | ... | ... | ... | ... | 15 | 10 |
| Aquarium, 7 days | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 17 |
| Aquarium, 14 days | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |

nents that have evaporated or dissolved in the water. Note that the stronger, broader bands remain unchanged.

The sampling time for the No. 2 fuel was 2 days. Since No. 2 fuel contains mainly light components, it is more difficult to match the weathering conditions of the three grids. This is the reason for the lack of the carbonyl band in the spectrum of the in-lab sample (*d*). The computer comparison of the Bay with the roof sample gave 17/18 ratios within 10% of the average, whereas comparison of the Bay with the laboratory sample had only 14/18 ratios within 10% of the average. The spectrum of a No. 2 fuel oil changes faster with weathering time than heavier oils, and in most cases, the oil disappears from the surface of water during the first week of weathering.

In all cases, we have been able to simulate weathering conditions in the laboratory and on the roof of the laboratory to match those of Narragansett Bay; however, as indicated above, the rate of change is difficult to duplicate. Temperature control, amounts of agitation and illumination are critical for the simulated weathering. Due to drastically different water temperatures between night and day in the roof weathering containers, we recently replaced this grid with the on-shore grid described in *ii*.

Comparison of Real and Simulated Oil Spills. To test the capability of our weathering grids to simulate actual conditions we have compared spectra of oil samples taken from an actual spill with those of the same oil weathered in our grids. On October 10, 1974, a tanker spilled 100 000 gal of No. 6 fuel oil into New Haven Harbor. We obtained a large sample from the tanker and samples from the spill after 1 and 6 days. The oil from the tanker was weathered in the grids during the same time to match conditions as closely as possible.

Infrared spectra of the unweathered oil and oil from the spill are shown in Figure 9. Even though this was a heavy oil, its spectrum did change upon weathering; thus, it was a good test for the weathering grids.

Spectra of the New Haven spill samples are compared to the original oil and to those weathered in our grids in Table III, where the number of normalized log-ratios within 0.04 (10%) of the average are given. The spectra of the spill samples did change from the original; however, they compared extremely well with the spectra of the samples weathered in our grids, indicating that artificial conditions give a reasonable simulation of an actual spill.

Conclusions

Our results on weathering 60 different oils in confined areas indicate that weathering alters the infrared fingerprints. However, natural weathering conditions can be simulated by weathering in containers on land or in the laboratory. Thus, it is possible to "match" oils from actual spills with those weathered artificially.

The major contributing factors to weathering are water and air temperatures, illumination, and agitation. All of these affect the rate of weathering; however, water temperature appears to play the major role during the initial weathering period.

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Associations of Chlorinated Hydrocarbons with Fine Particles and Humic Substances in Nearshore Surficial Sediments

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■ *p,p'*DDE generally accounts for 60–70% of the total chlorinated hydrocarbon content in sediment, whereas PCB's (mostly Arochlor 1254) constitute almost 10–20% of the total. Other isomers of DDT and dieldrin account for the remaining fraction. Concentrations of chlorinated hydrocarbons are closely related to the organic contents and to particles of 8 μm or less in size. Total organic carbons of sediments as well as fulvic and humic acid fractions bear a linear relationship with respect to concentrations of chlorinated hydrocarbons in sediments. Total chlorinated hydrocarbon contents of sediments studied range from 0.3 to 3.5 ppm, whereas total organic carbon contents range from 0.45 to 1.70% on a dry weight basis.

A considerable amount of work has been done on the adsorption of chlorinated hydrocarbons on humic substances, clays, or organoclay complexes. Ballard (1) reported that humic substances can act as carriers of DDT in the organic layer of a forest soil. Wershaw et al. (2), in studying the interaction of pesticides with natural organic materials, concluded that sodium humate can solubilize an otherwise insoluble insecticide, DDT, whereas humic acid strongly adsorbs 2,4,5-T from solution. The natural organic polyelectrolytes (humic substances) may also interact with other chlorinated hydrocarbons of similar structure. Recently, Pierce et al. (3) reported that suspended humic particulates may serve as transporting agents for chlorinated hydrocarbons through the water column and provide a mechanism for accumulation of chlorinated hydrocarbons in sediments.

In studying the adsorption of herbicides, Khan (4, 5) suggested that the mobility and persistence of 2,4-D in soils and waters will be partly a function of adsorption of the herbicide onto surfaces such as fulvic acid-clay complexes. And interactions of clay with organic matters may facilitate the adsorption of diquat and paraquat on clay minerals in soil. Fredeen et al. (6) found most of the DDT to be associated with suspended solids consisting mainly of clay and fine silts. McDermott et al. (7) indicated that sediments constitute by far the largest known local reservoir of chlorinated hydrocarbons along the southern California coast.

Since humic substances are the major components of the organic matter from marine sediments (8), and fine particle fractions, such as clay, in sediments are closely associated with organic matter in the form of organomineral complexes (9), efforts were made in this study to investigate the relations between chlorinated hydrocarbons and humic substances together with particle fractions finer than 8 μm in marine sediments.

Experimental

Collection of Sediment Samples. Sediment samples from Los Angeles Harbor along the Terminal Island sewer outfall to the breakwater entrance were collected by stainless steel Reinecke or Campbell grab sampler from the *Velero IV* and *Golden West*, ocean-going research vessels operated by the Hancock Foundation of the University of Southern California. Upon extrusion from cores, these sediment samples were sealed in plastic bags and stored in ice at 4 °C for transport to the laboratory, where the well-mixed subsamples were

transferred into an airtight plastic container in a glove bag under a nitrogen atmosphere. The samples were stored in a refrigeration unit at approximately 4 °C until used. The homogenized sediment from each station was split into three fractions to be extracted and/or analyzed for humic and fulvic acids, chlorinated hydrocarbons, and particle size.

Extraction of Humic Substances. Extraction of humic substances was generally performed in accordance with the method described by Kaplan and Nissenbaum (8). A 200-g sample of wet sediment was weighed into a 2-l. Teflon bottle, to which 1 l. of 0.1 N NaOH was added. Immediately, the Teflon bottle was purged with nitrogen and then sealed tightly. The sediment sample was shaken on a Burrell Model 75 wrist-action shaker for 5 h at room temperature. It was then rapidly centrifuged at 10 000 rpm, 18 °C, on an IEC Model B-20A high-speed centrifuge. The solids remaining were repeatedly extracted until the supernatant became virtually colorless—a process usually taking 2–5 l. of 0.1 N NaOH. All of the supernatant solutions from the successive extractions were then combined. An aliquot (200 ml) of the combined supernatant solutions was acidified with 5 ml of conc. HCl and left to stand for 96 h at room temperature. The fulvic acid (the supernatant of the acidified solution) was separated from the humic acid (precipitate) by centrifugation at 15 000 rpm. The humic acid precipitated in the acidified solution (pH = 0.7–1.2) was redissolved with 0.1 N NaOH.

Analysis of Organic Carbon. Organic carbon analysis was performed in four parts: organic carbon in the sediment sample, organic carbon in the combined supernatant solution through successive extractions with 0.1 N NaOH, organic carbon in the humic acid fraction, and organic carbon in the fulvic acid fraction. Organic carbon in the sediment was determined with a LECO Model TC-12 automatic carbon determinator. Prior to analysis, all sediment samples were treated with 6 N HCl to remove carbonates (10). Total carbon and total inorganic carbon on liquid samples of the combined supernatant solution, humic and fulvic acid fractions, were determined with a Beckman TOC analyzer, Model 915. Organic carbon on liquid sample was then determined by the difference (11).

Analysis of Chlorinated Hydrocarbons. The extraction, separation, identification, and quantification of chlorinated hydrocarbons were generally performed in accordance with the published literature (12–18). Details of the operation are described as follows.

Extraction. Acetonitrile, 250 ml (pesticide quality, Matheson Coleman & Bell), was added to the glass-stoppered flask containing 10 g of wet sediment, which was then shaken for 1 h on a reciprocal shaker. The flask was kept in a constant temperature chamber (14 ± 2 °C) overnight. The sample was again shaken for 2 h and then filtered through 5 g of Celite (Celite 545, Sargent Welch) media on Whatman No. 4 filter paper under mild vacuum. At this time, another 100 ml of acetonitrile was added to avoid the possible loss of chlorinated hydrocarbons on the container walls, Celite, or residue. The filtrate was transferred to a 500-ml Kuderna-Danish concentrator and concentrated to approximately 5 ml on a water bath. The concentrated filtrate was then transferred to a 1000-ml separatory funnel containing 200 ml of double-distilled water and 10 ml saturated NaCl solution. Petroleum ether, 80 ml (pesticide quality, Matheson Coleman & Bell),

was used to clean the concentrator and was added to the separatory funnel. The process was then repeated. After the third extraction, the aqueous phase was discarded, and all the petroleum ether extracts were collected into another Kuderna-Danish concentrator. After the extraction, petroleum ether was concentrated to approximately 5 ml and then eluted on the prepared activated florisil column.

Florisil Column Elution. A chromatographic tube (450 × 28 mm) with a removable frittered glass and Teflon stopcock was packed with 15 g of activated florisil (60/100 mesh, GC grade, Sargent Welch) which had been stored at 130 °C and topped with 15 g of anhydrous sodium sulfate (reagent grade, J. T. Baker) to absorb water from the extract. The column was then washed with 70 ml of petroleum ether. The petroleum ether extract (concentrated to approximately 5 ml) was added when the petroleum ether sank through the top surface of the anhydrous sodium sulfate. Sequential elutions were then carried out, first with 175 ml of petroleum ether, next with 100 ml of 6 vol % ethyl ether–94 vol % petroleum ether mixture (6 + 94), and finally with 150 ml of 15 vol % ethyl ether–85 vol % petroleum ether mixture (15 + 85). During the elution, flow rate was controlled by the Teflon stopcock at approximately 2 ml/min. By the florisil column elutions, polychlorinated biphenyls (PCB's) and most of the DDE were recovered in petroleum ether, most of other organochlorine compounds in 6 vol % ethyl ether–94 vol % petroleum ether mixture, and endrin and dieldrin in 15 vol % ethyl ether–85 vol % petroleum ether mixture. Each eluted sample was again concentrated, and the exact final volume was measured. Since sulfur was present in relatively large amounts in all sediment samples tested, every extract was treated with mercury (reagent grade, Quicksilver Products) to remove sulfur as mercuric sulfide before injection into the gas chromatograph.

Identification and Quantification. Standards of DDT series were supplied by Supelco, Inc., PCB standards (Arochlor) by Monsanto Chemical Co., and aldrin and dieldrin by Shell Chemical Co., all at 99.0–99.5% purity.

A Hewlett-Packard research gas chromatograph Model 5750 equipped with a Ni⁶³ electron capture detector was used throughout the study. The glass column (1220 × 4 mm) was packed with 5% QF-1 (Chromosorb W-HP, 80/100 mesh, Sargent Welch). The carrier gas used was prepurified 95% argon and 5% methane mixture. The flow rate of the carrier gas was maintained at approximately 25 ml/min. The operating temperatures were 210 °C for the oven, 235 °C for the injection port, and 265 °C for the detector. The retention times (relative to aldrin) and detection limits of chlorinated hydrocarbons are listed in Table I.

The sample components were identified by comparison of retention times of unknown peak to the known peaks of reference standard solutions and were quantified by comparison of the peak height of the identified component to the peaks of the component in the reference standard solution. In addition to the single-component reference standard solutions, multicomponent standard solutions with different combinations and components were prepared. Preliminary sample injections were always performed to determine whether pre-concentration or dilution of the sample was needed, as well as the series of reference standard solutions to be used.

The efficiencies of recovery found after spiking 10 g of wet sediments with 0.1–1.0 µg of chlorinated hydrocarbons are: 85–99% for DDT homologs, 85–94% for dieldrin, and 93–102% for PCB's. These figures are less than those reported by Goerlitz and Law (21), but comparable to those of Woolson (22).

Dehydrochlorination of Chlorinated Hydrocarbons in Alkaline Solution. Dehydrochlorination of DDT occurs in alkali solutions (20). Since the purpose of this study was the association of humic substances and chlorinated hydrocar-

bons, it was essential to evaluate the occurrence and extent of dehydrochlorination of chlorinated hydrocarbons. As the extraction of humic substances was performed with 0.1 N NaOH at room temperature, a synthetic study of dehydrochlorination of chlorinated hydrocarbons by 0.1 N NaOH was carried out. The kinetics of dehydrochlorination were studied over a period of 48 h.

Twenty-five milliliters of 10 ppm chlorinated hydrocarbon solution in acetonitrile was added to 225 ml of 0.1 N NaOH in a 500-ml volumetric flask. The flask was then stoppered and stirred on a magnetic stirrer (Lab-Line Multi-Magstir) at room temperature (21 ± 2 °C). Reactions were then terminated at time intervals of 1, 5, 12, 24, and 48 h. Blanks were run in all cases. Immediately after each stirring period, chlorinated hydrocarbons were extracted from the solution by shaking for 5 min with three 80-ml aliquots of petroleum ether and made up to a volume of 250 ml by adding petroleum ether. This is further diluted with petroleum ether before injection into the gas chromatograph.

Analysis of Particle Size. A portion of an homogenized sediment sample was pretreated with 30% H₂O₂ (reagent grade, Matheson Coleman & Bell) to remove organic matter. Sodium hexametaphosphate—(NaPO₃)₆ (J. T. Baker—solution, 6.0 g/l., was used as a dispersing agent. After wet-sieving the sample (U.S. STD No. 230 sieve), the particles of the fine fraction (≤62 µm) were further analyzed in accordance with the pipet method (23).

Results and Discussion

The study of dehydrochlorination has shown that several chlorinated hydrocarbons such as DDE, dieldrin, and PCB's (Arochlor 1242, 1254, and 1260) were unchanged by the alkaline attack within a 48-h period. However, DDT and DDD were considerably dehydrochlorinated during the test period. Data on the dehydrochlorination of DDT and DDD can be plotted to fit first-order reactions as shown in Figure 1. Reaction rate constants (*k*) obtained by the slopes of straight lines in Figure 1 and half lives (*t*_{1/2}) calculated from the first-order equation, as well as the expected products formed by dehydrochlorination, are shown in Table II. The use of 0.1 N NaOH during the humic substance extraction would cause

Table I. Retention Times Relative to Aldrin and Detection Limits of Some Chlorinated Hydrocarbons

| Chlorinated hydrocarbon | Retention time ^a | | Detection limit, pg |
|-------------------------------|-----------------------------|------|---------------------|
| | (a) | (b) | |
| Aldrin | 1.00 | 1.00 | 5 |
| Dieldrin | 2.71 | 2.22 | 10 |
| <i>p,p'</i> DDT | 3.38 | 3.28 | 25 |
| <i>o,p'</i> DDT | 2.34 | 2.48 | 20 |
| <i>p,p'</i> DDD | 3.12 | 2.70 | 10 |
| <i>o,p'</i> DDD | 2.18 | 2.04 | 15 |
| <i>p,p'</i> DDE | 1.88 | 1.88 | 10 |
| <i>o,p'</i> DDE | 1.42 | 1.46 | 30 |
| <i>p,p'</i> DDMU ^b | 1.54 | 1.50 | ... |
| <i>o,p'</i> DDMU ^b | 1.24 | 1.21 | ... |
| PCB 1242 | ... | ... | 150 |
| PCB 1254 | ... | ... | 150 |
| PCB 1260 | ... | ... | 250 |

^a (a) This study, (b) Brooks (20), page 81, Table 11. ^b Relative retention times of *p,p'*DDMU and *o,p'*DDMU were calculated from the peaks appearing after dehydrochlorination reaction of *p,p'*DDD and *o,p'*DDD with 0.1 N NaOH. DDMU is formed by dehydrochlorination of DDD with NaOH (19). Relative retention times of the peaks shown are very close to those of the other study, as shown in Table I. No attempt was made to confirm products formed by dehydrochlorination of DDD.

considerable dehydrochlorination of some chlorinated hydrocarbons in sediments and may also cause modification of the adsorptive properties of organomineral complexes. A direct experimental approach to differentiate chlorinated hydrocarbons in each organic fraction (humic acid, fulvic acid, and others) would be untenable.

The results of the quantification of organic carbon in sediment, humic substances, and humic and fulvic acid fractions are listed in Table III. Of seven sediment samples studied (each collected from a different location), organic carbon of the humic substances, $\text{TOC}_{(\text{NaOH})\text{sx}}$, can account for only 11–68% of the total organic carbon in the sediment (TOC_{sed}), with most found between 25–35%. This indicates that the remaining fractions—refractory organics and lipids, among others—are still the predominant source of organic carbon in sediment. In addition, the remaining organic carbon also contains humin fraction, which is not extractable with alkali solution.

Extraction of the humus from soil with alkali has been reported to remove only about one-third of the actual amount (24). On the other hand, Schnitzer and Khan (25) claimed that the dilute aqueous NaOH solution is quantitatively the most effective reagent for extracting humic substances from sediments and soils. In this study, humic substances from sediments were extracted successively with 0.1 N NaOH until the supernatant became nearly colorless. However, the actual

amount of humic substances present in the sediment is still unknown. For instance, the humin fraction (which is part of humic substances) is known to be insoluble in sodium hydroxide (26). Therefore, it is reasonable to assume that $\text{TOC}_{(\text{NaOH})\text{sx}}$, TOC_{HA} , and TOC_{FA} data listed in Table III are on the lower end of the scale.

The relations of fine particles in the sediments to the total organic carbon contents of sediments, as well as fulvic and humic acid fractions, are shown in Figures 2–4. This is similar to the report that the amount of organic material in surficial sediments was directly proportional to the clay-size fraction (less than 2 μm) of sediment (27).

The contents of chlorinated hydrocarbons in sediments are shown in Table IV. The data show that *p,p'*DDE constitutes 61–71% of the total DDT. Other isomers are: *o,p'*DDE, 6.1–9.1%; *p,p'*DDD, 10.0–16.6%; *o,p'*DDD, 3.4–7.8%; *p,p'*DDT, 2.8–7.7%; and *o,p'*DDT, 2.6–4.6%. The results are quite similar to those of recent studies (7, 28). Dieldrin constitutes less than 1% of the total chlorinated hydrocarbon content (total DDT + dieldrin + PCB's). For Stations 6 and 7, which are located in the proximity of a sewer outfall, the percentage of PCB's is very high, from 45–65% of the total chlorinated hydrocarbon content. For the rest of the stations, total DDT and PCB's (mostly Arochlor 1254) constitute 87–92% and 8–19% of the total chlorinated hydrocarbons, respectively.

Figures 5 and 6 show that the concentrations of both total DDT and total chlorinated hydrocarbons increase with increasing contents of total organic carbon in the sediment samples. This is similar to the results taken from Southern Lake Michigan on the accumulation of total DDT in lake sediments (27). O'Connor and Anderson (29) recently reported that the organic matter was an important contributor to 2,4,5-T adsorption, and in some soils might be the only adsorbent of significance. They also stated that the amount of the herbicide adsorbed per gram of organic matter was not constant, but adsorption tended to increase with organic matter. Figures 5 and 6 show that total DDT and total chlorinated hydrocarbons increase with increasing $\text{TOC}_{(\text{NaOH})\text{sx}}$, TOC_{HA} , and TOC_{FA} . This may indicate the significance of humic substances for the adsorption of chlorinated hydrocarbons. These results are reasonable in view of other studies (1–5, 30). However, chlorinated hydrocarbons in the sediment may not only be influenced by the amount of organic matter, but also by other factors such as particle size distributions in the sediments.

Ballard (7) reported that in DDT-spiked humic extracts (HA + FA), 91% of the added *o,p'*DDT was recovered in humic acids, and the remaining 9% was recovered in fulvic acids plus water, indicating that humic acids are much more capable of adsorbing DDT than fulvic acids. Recently, Khan (4) investigated the adsorption of 2,4-D from aqueous solution by fulvic acid-clay complex (38 + 62%) and found that about 6.5 and 5.2 μmol of 2,4-D were adsorbed per gram of the complex at 5 and 25 $^{\circ}\text{C}$, respectively. Furthermore, results of this study (Table III) show that in most sediments tested, the fulvic acid

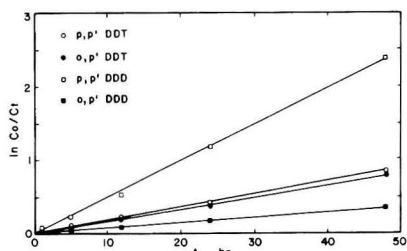


Figure 1. Dehydrochlorination of chlorinated hydrocarbons in 0.1 N NaOH

Table II. Dehydrochlorination of DDT and DDD at 21 \pm 2 $^{\circ}\text{C}$ and at pH = 12.8 (0.1 N NaOH)

| Reactant ^a | Product | k , h^{-1} | $t_{1/2}$, h |
|-----------------------|------------------|-----------------------|---------------|
| <i>p,p'</i> DDT | <i>p,p'</i> DDE | 1.75×10^{-2} | 39.6 |
| <i>o,p'</i> DDT | <i>o,p'</i> DDE | 1.65×10^{-2} | 42.0 |
| <i>p,p'</i> DDD | <i>p,p'</i> DDMU | 5.00×10^{-2} | 13.9 |
| <i>o,p'</i> DDD | <i>o,p'</i> DDMU | 0.76×10^{-2} | 96.3 |

^a Reactant concentration = 1.0 ppm in 0.1 N NaOH.

Table III. Organic Carbon in Total Sediment, Humic Substances, and Humic and Fulvic Acid Fractions

| Sediment no. | Dry wt of sediment used for extraction of organics, g | Vol of 0.1 N NaOH used for successive extractions, l. | TOC_{sed} , dry wt | $\text{TOC}_{(\text{NaOH})\text{sx}}$ | | TOC_{HA} | | TOC_{FA} | | $\text{TOC}_{(\text{NaOH})\text{sx}}/\text{TOC}_{\text{sed}}$, % | $\text{TOC}_{\text{HA}}/\text{TOC}_{\text{sed}}$, % | $\text{TOC}_{\text{FA}}/\text{TOC}_{\text{sed}}$, % |
|--------------|---|---|------------------------------------|---------------------------------------|----------|--------------------------|----------|--------------------------|----------|---|--|--|
| | | | | mg/l. | % dry wt | mg/l. | % dry wt | mg/l. | % dry wt | | | |
| 1 | 155.4 | 5 | 0.51 | 41 | 0.132 | 6 | 0.019 | 36 | 0.116 | 25.9 | 3.7 | 22.7 |
| 2 | 109.0 | 5 | 1.43 | 110 | 0.505 | 50 | 0.229 | 77 | 0.353 | 35.3 | 16.0 | 24.7 |
| 3 | 132.8 | 5 | 0.83 | 77 | 0.290 | 26 | 0.098 | 47 | 0.177 | 34.9 | 11.8 | 21.3 |
| 4 | 142.2 | 5 | 0.65 | 64 | 0.225 | 17 | 0.060 | 41 | 0.144 | 34.6 | 9.2 | 22.2 |
| 5 | 132.8 | 5 | 0.87 | 64 | 0.241 | 32 | 0.120 | 37 | 0.139 | 27.7 | 13.8 | 16.0 |
| 6 | 162.0 | 2 | 0.45 | 41 | 0.051 | 9 | 0.011 | 32 | 0.040 | 11.3 | 2.4 | 8.9 |
| 7 | 127.2 | 3 | 1.71 | 490 | 1.156 | 390 | 0.920 | 270 | 0.637 | 67.6 | 53.8 | 37.3 |

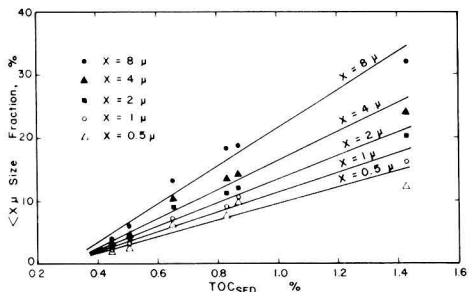


Figure 2. Relationship of particle size and total organic carbon in sediments

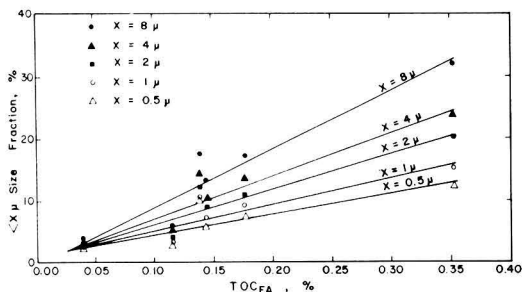


Figure 3. Relationship of particle size and organic carbon of fulvic acid fraction in marine sediments

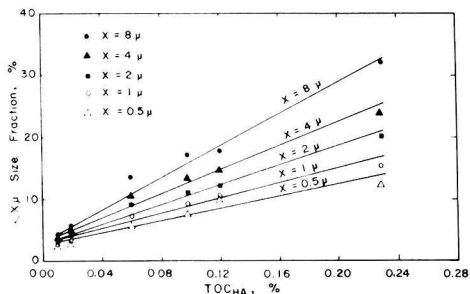


Figure 4. Relationship of particle size and organic carbon of humic acid fraction in marine sediments

fraction generally exceeds the humic acid fraction. From Figures 5 and 6, fulvic acids also behave as one of the potential adsorbents for chlorinated hydrocarbons in the sediments. Numerous workers (4, 9, 31, 32) have reported the direct relationship of the contents of organic matter and clay size particles. Since concentrations of chlorinated hydrocarbons are related to organic matter, particularly to humic substances, a strong relation between very fine grain size fraction in the sediments and chlorinated hydrocarbons is also implied.

Results of this study suggest that the fraction of very fine silts and clays ($\leq 8 \mu\text{m}$) and the amount of humic substances are important factors in controlling the adsorption capacity of chlorinated hydrocarbons in marine sediments. From Figures 2-4, fine silt and clay particles are closely associated with organic matter such as humic substances existing in the form of organomineral complexes. This intimate adsorptive association causes modification of the particle surfaces or adsorptive properties of humic materials.

Summary

From the literature, fine silts and clays in sediments are closely associated with humic substances and exist in the form of organoclay complexes. The data presented herein show that a linear relationship exists between the concentration of chlorinated hydrocarbons and total organic carbon, within a range of up to $8 \mu\text{m}$. This type of linear relationship also exists between chlorinated hydrocarbons and carbon fractions due to fulvic and humic acid. All these factors suggest a possible association of humic substances with chlorinated hydrocarbons. These types of associations and the colloidal behavior of the organoclay complexes may explain recent findings (33, 34) that the transfer of chlorinated hydrocarbons from sediments to the solution phase is negligible under most laboratory conditions.

Acknowledgment

The authors are grateful to Miroslav Z. Knezevic for his comments and suggestions.

Nomenclature

- 2,4-D = 2,4-dichlorophenyl acetic acid
- 2,4,5-T = 2,4,5-trichlorophenoxy acetic acid
- aldrin = 1,2,3,4,10,10-hexachloro-1,4,4,5,8,8 α -hexahydro-1,4-endoexo-5,8-dimethanonaphthalene
- dieldrin = 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4,5,6,7,8,8 α -octahydro-1,4-endoexo-5,8-dimethanonaphthalene
- diquat = 1,1-ethylene-2,2-bipyridylum dibromide
- paraquat = 1,1-dimethyl-4,4-dipyridylum dichloride
- p,p' DDT = 1,1,1-trichloro-2,2-bis(p -chlorophenyl)ethane

Table IV. Concentrations of Chlorinated Hydrocarbons in Marine Sediments

| Sediment no. | Moisture content, % | p,p' DDE/ t -DDT, % | o,p' DDE/ t -DDT, % | p,p' DDD/ t -DDT, % | o,p' DDD/ t -DDT, % | p,p' DDT/ t -DDT, % | o,p' DDT/ t -DDT, % | Total DDT, ^a ppm | Dieldrin, ppb | Total PCB's, ppm | Total chlor. hydrocarbs., ppm |
|--------------|---------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-----------------------------|---------------|------------------|-------------------------------|
| 1 | 22.3 | 71.0 | 6.3 | 10.6 | 6.0 | 2.8 | 3.2 | 0.321 | 0.9 | 0.046 | 0.368 |
| 2 | 45.5 | 69.6 | 7.1 | 10.0 | 5.2 | 5.0 | 3.1 | 3.212 | 1.3 | 0.285 | 3.498 |
| 3 | 33.6 | 65.9 | 9.1 | 10.8 | 6.4 | 3.1 | 4.6 | 0.831 | 0.9 | 0.123 | 0.955 |
| 4 | 28.9 | 68.6 | 8.2 | 10.2 | 6.2 | 2.8 | 4.0 | 0.353 | 0.6 | 0.05 | 0.403 |
| 5 | 33.6 | 62.0 | 8.4 | 14.5 | 3.4 | 7.7 | 4.0 | 0.297 | 2.2 | 0.071 | 0.370 |
| 6 | 19.0 | 61.7 | 8.7 | 12.2 | 7.8 | 7.0 | 2.6 | 0.115 | 2.1 | 0.190 | 0.307 |
| 7 | 36.4 | 60.7 | 6.1 | 16.6 | 6.1 | 6.5 | 4.0 | 0.247 | 4.5 | 0.214 | 0.466 |

^a Total DDT = sum of all DDT, DDE, and DDD.

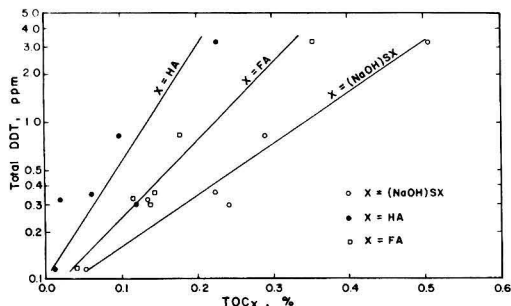


Figure 5. Relationship of total organic carbon and total DDT in marine sediments

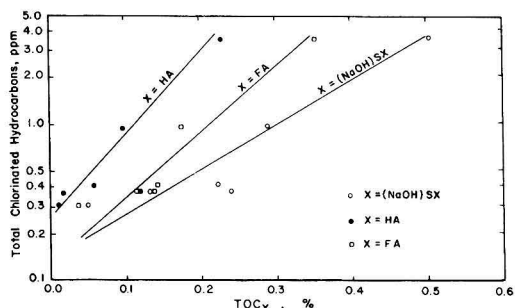


Figure 6. Relationship of organic carbon and total chlorinated hydrocarbons in marine sediments

- o,p' DDT = 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane
 p,p' DDD = 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethane
 o,p' DDD = 2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)-1,1-dichloroethane
 p,p' DDE = 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene
 o,p' DDE = 1,1-dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene
 p,p' DDMU(p,p' DDD-olefin) = 2,2-bis(*p*-chlorophenyl)-1-chloroethylene
 o,p' DDMU(o,p' DDD-olefin) = 2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)-1-chloroethylene
 PCB 1242 = Arochlor 1242, $C_{12}H_6Cl_{13}$
 PCB 1254 = Arochlor 1254, $C_{12}H_5Cl_5$
 PCB 1260 = Arochlor 1260, $C_{12}H_3.7Cl_{6.3}$
 C_o = initial molar concentration of chlorinated hydrocarbon (reactant), μmol
 C_t = molar concentration of chlorinated hydrocarbon (reactant) at time t , μmol
 t = reaction time, h
 TOC_{FA} = total organic carbon in fulvic acid fraction, mg/l.
 TOC_{HA} = total organic carbon in humic acid fraction, mg/l.
 $\text{TOC}_{(\text{NaOH})\text{SX}}$ = total organic carbon in combined supernatant solution, successively extracted with 0.1 N NaOH, mg/l.
 TOC_{sed} = total organic carbon in the sediment sample, % dry wt
 $(\text{NaOH})\text{sx}$ = total amount of organic carbon obtained through successive extraction with 0.1 N NaOH

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Long-Path Infrared Spectroscopic Investigation at Ambient Concentrations of the 2% Neutral Buffered Potassium Iodide Method for Determination of Ozone

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■ Following disclosure by the California Air Resources Board (ARB) and the Los Angeles Air Pollution Control District (LAAPCD) of a significant discrepancy (~30%) between their respective ozone calibration procedures, we investigated the stoichiometry of the 2% neutral buffered potassium iodide (NBKI) method for ozone (ARB method). An environmental chamber with an in-situ long-path optical system was employed to simultaneously obtain infrared (IR) spectra and 2% NBKI impinger samples over a range of ozone concentrations (0.1–1.2 ppm) encompassing ambient levels at several relative humidities (RH). Absolute ozone concentrations were calculated from the well-resolved $9.48 \mu\text{R}$ -branch absorption of ozone using an absorptivity of $4.23 \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1}$ RTP which was experimentally determined by two independent methods. Linear regression analyses of the 2% NBKI and IR ozone concentrations yielded: $[\text{O}_3]^{\text{KI}} = 1.14[\text{O}_3]^{\text{IR}} + 0.013$ for 3% RH, $[\text{O}_3]^{\text{KI}} = 1.12[\text{O}_3]^{\text{IR}} + 0.001$ for ~18% RH, $[\text{O}_3]^{\text{KI}} = 1.23[\text{O}_3]^{\text{IR}} + 0.001$ for 50% RH. Although the dependence on RH is not understood, these results indicate that the 2% NBKI method yields ozone concentrations 12–14% higher than the absolute spectroscopic determinations at low RH, and 23–25% higher at high RH. In the course of this investigation, a collaborative study with W. B. DeMore demonstrated excellent agreement between simultaneous measurements of ozone samples by IR and UV spectroscopies where the absorptivities employed were $4.23 \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1}$ and $135 \text{ cm}^{-1} \text{ atm}^{-1}$, respectively.

In June 1974 it was revealed by the California Air Resources Board (ARB) (1, 2) that a systematic and significant (~30%) discrepancy existed between the ozone calibration procedures employed by the Los Angeles County Air Pollution Control District (LAAPCD) and the methods used by other California APCD's, the ARB, and the U.S. Environmental Protection Agency (EPA). While the LAAPCD utilized a 2% *unbuffered* potassium iodide (KI) absorbing solution and a visual end-point titration for calibration (3), the other agencies employed 1% (EPA) or 2% (ARB) neutral *buffered* KI absorbing solutions and a colorimetric end-point determination in their calibration procedures (4–6). The announcement that oxidant measurements made by the LAAPCD were approximately 30% lower (1, 2) than equivalent measurements made by other agencies in the South Coast Air Basin has caused significant difficulties for control officials concerned with the establishment of basin-wide health warning alert systems and the implementation of oxidant control strategies (7), as well as for atmospheric scientists attempting to develop models describing pollutant transport in the California South Coast Air Basin (8). Additional ramifications of the reported discrepancy in oxidant measurement methods and corrections of past ambient oxidant data from the LAAPCD, other counties' APCD's, and ARB air monitoring stations in the South Coast Air Basin to obtain an internally consistent set of data for the Basin as a whole are presented in a companion paper (9).

It should be noted at the outset that all three calibration procedures discussed above respond, with varying stoichiometries, to compounds other than ozone, including both oxidizing and reducing species. For example, SO_2 causes a 100% negative response, whereas NO_2 causes a 5–10% positive response (6). However, under controlled laboratory conditions in which only ozone is present (or through the use of scrubbers for interfering species), direct comparison of the methods with respect to response to ozone is possible. It is also possible under these conditions to determine whether the wet chemical potassium iodide methods are in agreement with measurements of ozone concentrations by physical methods, such as UV or IR spectroscopy. These in-situ spectroscopic methods can be related to primary determinations for ozone, for example, absolute pressure measurements.

To our knowledge, physical measurement methods such as UV or IR spectroscopy had not been applied to investigations of the 2% unbuffered KI (LAAPCD) or 2% buffered KI (ARB) methods prior to the discovery of the discrepancy between these methods. In contrast, the 1% neutral buffered KI method specified (5) by the EPA as the calibration procedure for instruments measuring oxidant or ozone had been extensively investigated. These investigations followed a report by Boyd and coworkers (10) that at high (>100 ppm O_3 in O_2) concentrations, they obtained (from UV photometric measurements) a ratio of 1.5 mol iodine released per mol of ozone absorbed in 1% neutral buffered reagent, thus calling into question the 1:1 stoichiometry previously assumed for this method. However, in subsequent investigations by Kopczynski and Bufalini (11) (using infrared absorption spectroscopy), by Hodgson et al. (12) (using gas-phase titration of ozone with nitric oxide in air), and by Behl (13) (using a Kruger-type ozone photometer), all reported a 1:1 stoichiometry for the 1% neutral buffered method within their experimental uncertainties.

In view of the ramifications of the reported discrepancy between the buffered and unbuffered 2% KI methods, and the conflicting reports in the literature concerning the stoichiometry of the 1% NBKI method, as well as our use of the 2% neutral buffered method in calibrating the various ozone analyzers employed in our laboratories and air monitoring sites, we began an investigation of the stoichiometry of the 2% neutral buffered KI method at *ambient* concentrations using long-path infrared (LPIR) spectroscopy. Although our infrared study of the ARB reference method was similar in principle to that of Kopczynski and Bufalini (11) (for the 1% NBKI method), it differed significantly in two important respects. First, the majority of our data were obtained for ozone concentrations below 1 ppm (i.e., at ambient levels), whereas their lowest determination was for 2 ppm of ozone. Secondly, the absorptivity we employed was determined for absolute ozone samples under the precise spectroscopic conditions used in our KI study, whereas Kopczynski and Bufalini employed an absorptivity determined [by Hanst et al. (14)] for spectroscopic conditions which could have differed from those used in their KI study. We report here the results of our investigation and our conclusions concerning the validity of the 2% neutral buffered KI method for the measurement of ozone in air monitoring applications.

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Infrared Measurements. For sensitivity in the fractional part per million (ppm) range, an in-situ multiple reflection cell [based on the design of White (15) and of Horn and Pimentel (16)] was employed in a 5800-l. evacuable environmental chamber which has been described in detail elsewhere (17). The gold-coated multiple reflection optics were coupled to a spectrometer consisting of a Nernst glower source, a 1-m scanning monochromator (Interactive Technology Inc., Model CT103) employing a 75 line/mm grating blazed at 8.0μ , and a Santa Barbara Research Center mercury-cadmium-telluride detector ($2 \text{ mm} \times 0.5 \text{ mm}$, $D^* = 7.4 \times 10^{19}$) operated at 77 K. The infrared beam was chopped at 1100 Hz, and the preamplifier (Princeton Applied Research Model 118) output was carried to a PAR Model 126 lock-in amplifier operating at a 3-kHz bandpass. Figure 1 shows a schematic of the environmental chamber with its in-situ long-path cell and the infrared spectrometer.

All spectra were obtained at a path length of 69.2 m and a spectral slit width of approximately 1.3 cm^{-1} . In this work, spectral slit width was defined as follows: For spectra obtained with a Perkin-Elmer Model 621 spectrophotometer (see below), spectral slit width was calculated from the mechanical slit width using data provided by Perkin-Elmer (18), whereas for spectra obtained with the Interactive Technology monochromator, spectral slit width was calculated by comparison to the Perkin-Elmer 621 spectra using the ratio of "valley" to "peak" absorbances as discussed below.

The spectral region from 8.80 to 10.40μ was scanned in 8.0 min using time constants of either 1.0 or 0.3 s. Thus, the scan rate was equivalent to 5 or 15 time constants per resolution element, more than sufficient in either case for photometric accuracy. The spectral region scanned included wavelengths about 0.3μ to both the long and short wavelength sides of the $9.6\text{-}\mu$ ozone band. A sample spectrum recorded for an ozone concentration of 6 ppm is shown in Figure 2. The well-resolved 9.48- μ R-branch was used to derive quantitative data.

Background (I_o) spectra were taken both before the introduction of ozone into the chamber and after a complete flushing at the end of the runs. No changes occurred in these spectra over the course of the run. All spectra were normalized at the spectrally clear wavelength of 8.822μ , thus assuring the applicability of the I_o spectra to all of the ozone spectra without ordinate correction in either sample or background spectra.

Ordinate scale expansions of $\times 5$ and $\times 10$ were used when measuring absorptions less than or equal to about 5%. The results from several scale-expanded spectra were compared with nonexpanded spectra taken as soon as possible before and after the scale expansion. The ozone concentrations deduced from these replicate measurements at ozone concentration between 2 and 0.6 ppm differed by 1–5% depending on the concentration. We attribute much of this small difference to the inability to measure the nonexpanded spectra of these weak absorptions to better than about 2 or 3% in ozone concentrations.

The photometric accuracy of the scale expansion was checked before and after each expanded spectrum by recording at least two transmission values in both the expanded transmission region and the normal scale. In general, the expanded transmission scale was accurate to 0.05% with a correctable I_o offset of no more than 0.2%. ($I_o - I$) was not sensitive to this correction and was known to at least $\pm 0.1\%$.

Matching the background to the ozone spectra on the wavelength axis was accomplished using eight weak, isolated water absorption lines in the region 8.8–9.4 μ . The transmission scale was matched as explained above by single wavelength normalization before taking spectra. This resulted in

excellent intensity match between the background and ozone spectra for all spectrally clear regions on both sides of the ozone absorption.

The 9.48- μ peak in the ozone band was reproducibly found by counting interference fringes present due to the 7.47- μ blocking filter used with the monochromator. As shown in Figure 3, obtained for an ozone concentration of 0.36 ppm, these fringes are just resolved in both background and ozone spectra, thus ensuring accurate wavelength determination for the intensity (I and I_o) measurements. The large baseline slope observed in Figure 3 results from multiplication of the changing HgCdTe detector response in this wavelength region by the $\times 10$ scale expansion. However, even for the lowest ozone concentrations and hence weakest absorptions, identification of the 9.48- μ wavelength was made unambiguously by counting the interference fringes.

The absorptivity of the 9.48- μ band appropriate to these studies was determined by two different methods (19). In the first, the dependence of the absorptivity at 9.48μ on spectral slit was determined over a range encompassing the spectral slit employed in this study and that employed by Hanst et al.

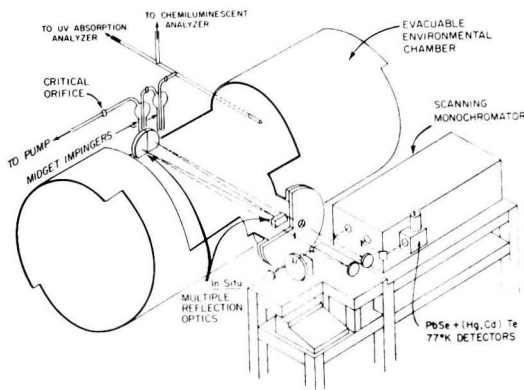


Figure 1. Schematic of environmental chamber and infrared spectrometer with in-situ long-path optical system (not to scale)

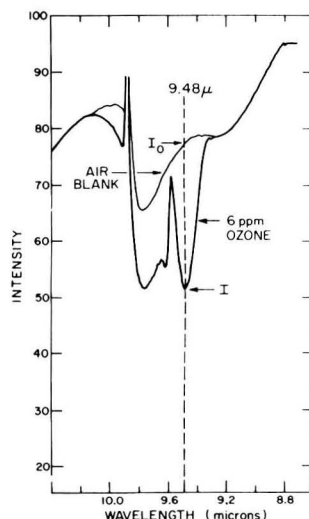


Figure 2. Ozone absorption band centered at 9.6μ showing R-branch at 9.48μ used to determine ozone concentrations

(14), in their absolute determination of the 9.48- μ band absorptivity. A Perkin-Elmer Model 621 spectrophotometer was used to make an extensive series of measurements at torr pressures of ozone in a 6-cm cell for spectral slit widths ranging from 0.9 to 9.9 cm^{-1} , and for fractional absorptions at 9.48 μ of 0.09, 0.26, 0.38, and 0.48.

Since a trapezoidal slit function (entrance slit = 0.75 mm, exit slit = 1.75 mm) was used for the NBKI comparison experiments, in order to enhance the photometric accuracy for our scan conditions, while the study of spectral slit vs. absorbance was performed on an instrument that could only be set with equal slits (i.e., triangular slit function), we felt it necessary to experimentally verify the theoretical condition

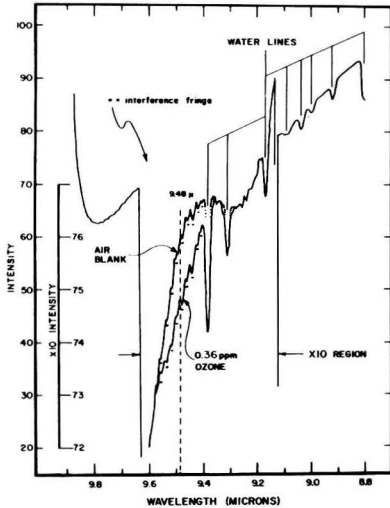


Figure 3. Scale expanded spectrum for 0.36 ppm ozone exhibiting water absorptions and interference fringes from which precise wavelengths were determined. Steep baseline slope in 9.48- μ region is due to multiplication of changing HgCdTe detector response by $\times 10$ scale expansion

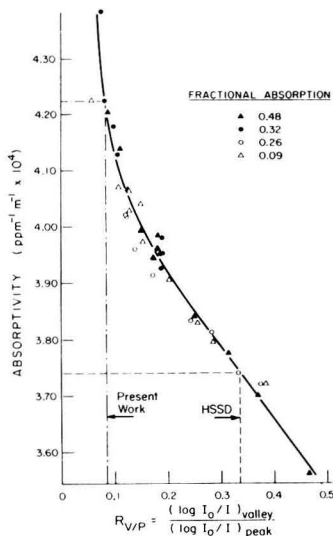


Figure 4. Dependence of absorptivity of ozone at 9.48 μ on spectral resolution (see text)

that, for a given spectral slit, the measured absorption is independent of slit shape. For entrance slits ranging from 0.750 to 2.128 mm and exit slits from 0.750 to 1.285 mm, the standard deviation of the absorbance was only 1.2% of the average at the 9.48- μ peak. Therefore, the extrapolation of data from triangular to trapezoidal slit function was shown to be valid at constant spectral slit for the experimental conditions of this study.

The results of the study of spectral slit (resolution) vs. absorptivity at 9.48 μ are presented in Figure 4. The abscissa variable chosen to represent resolution is the ratio of the absorbance at the absorption minimum (valley) between the *R* and *Q* branches to the maximum absorbance of the *R* branch (peak). The data obtained show that there is a linear relation between the ratio of absorbances ($R_{v/p}$) and spectral slit over the range $0.07 \leq R_{v/p} \leq 0.45$ which is independent of absorbance (19). Thus, by merely measuring $R_{v/p}$ for any ozone spectrum, the proper absorptivity may be determined directly from the data given in Figure 4. Our most careful measurements of the spectrum published by Hanst et al. (14) give a value for $R_{v/p}$ of 0.334. This value for $R_{v/p}$ along with their absorptivity of $3.74 \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1}$ RTP was used to normalize the ordinate scale in Figure 4 for each fractional absorption studied. $R_{v/p}$ for the present work, 0.086 ± 0.003 , gives a value for the absorptivity of $(4.23 \pm 0.05) \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1}$ RTP (25 $^{\circ}\text{C}$; 735 torr).

In a second study described in detail elsewhere (19), an absolute ozonizer was constructed, and ozone samples, whose concentrations were determined from absolute pressure-volume measurements, were admitted to the evacuable chamber, and the absorptivity of the 9.48- μ band was determined for concentrations of ozone of approximately 1 ppm, a pathlength of 69.2 m, and a spectral slit of approximately 1.3 cm^{-1} yielded an absorptivity of $(4.23 \pm 0.04) \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1}$ yielded an absorptivity of $(4.23 \pm 0.04) \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1}$ RTP (25 $^{\circ}\text{C}$; 735 torr). The absorptivity obtained was in excellent agreement with the value determined from the study of the dependence on spectral slit, and hence all ozone concentrations from infrared measurements reported in this paper were derived using an absorptivity of $4.23 \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1}$ RTP.

Preparation of Ozone Samples. In the initial experiment, a 5.4-l. bulb was filled to 1 atm pressure with an $\sim 1\%$ ozone-in-oxygen stream for a Welsbach ozonizer. The contents of the bulb were then flushed with nitrogen into the environmental chamber which had already been filled to 1 atm pressure (733 torr) with purified air (20) at 298.5 K. The resulting ozone concentration in the chamber was approximately 10 ppm, which was usually immediately reduced to ~ 2 -5 ppm by flushing the chamber with pure air. The strong absorption at 9.6 μ from this high ozone concentration was used to optimize the infrared scanning parameters and other experimental conditions. To study successively lower concentrations below 2 ppm, the chamber was flushed for specified lengths of time with additional pure air. After each flush the chamber contents were allowed to equilibrate as shown by constant ozone concentrations measured by both UV absorption (Dasibi) and chemiluminescence (Monitor Laboratories) ozone analyzers which were employed as convenient monitors of relative ozone levels during the experiment. Data obtained with these instruments also permitted calculation of the average ozone decay rate due to decomposition at the chamber walls and sampling losses. This rate ($k = 8.0 \times 10^{-4} \text{ min}^{-1}$) was used to make small corrections necessary to normalize the KI and LPIR ozone determinations to the same point in time as discussed below.

In succeeding experiments the ozone sample was made up in a 0.5-l. bulb and flushed into the chamber to produce an

ozone concentration of 1.0 ppm. This sample was then successively diluted as before to study lower concentrations.

2% Neutral Buffered Potassium Iodide Measurements. 2% KI absorbing reagent buffered at pH 6.89 was supplied by the ARB. Solutions were kept cool and in dark containers and were not more than four weeks old when used. To obtain an ozone measurement, 20 ml of this reagent was pipetted into each of two all-glass impingers which were connected in sequence via ungreased ball joints to a carbon vane pump at one end and a sample probe in the evacuable chamber at the other (see Figure 1). A critical orifice was used to ensure a constant sample flow rate of approximately 1 l./min, and the precise rate was accurately calibrated against a bubble meter. With knowledge of the flow rate, sample times (5, 10, or 24 min) were measured on a stopwatch to obtain exact sample volumes. For the studies carried out at 3% and 50% RH, sampling periods were either 5 or 10 min, and 10 ml of reagent was used in the impingers. For the study conducted at ~18% RH, sample periods were 24 min, and 20 ml of reagent was employed. No dependence of measured ozone concentration on sampling period was observed in this investigation. In all but one study the impinger samples were read after 3–5 min. Data obtained in a study in which the samples were allowed to develop for 30–50 min were subsequently corrected to 4 min after establishing the dependence of absorbance on time over a period of 1 h.

The samples were read on a Bausch and Lomb Spectronic 20 spectrophotometer at 350 nm. Two matched cells were used for the sample and a blank consisting of unreacted absorbant solution. The absorbances were converted to ozone concentrations using a calibration function supplied by the ARB. The resulting ppm (at 760 torr and 298 K) concentrations were corrected to the respective pressures and temperatures of the

experiments described below. For concentrations of ozone above 0.55 ppm, samples were diluted (4) by pipet in the ratios 1–3 or 1–2, so that all absorbances were less than 0.5, and the corresponding ozone concentrations could be interpolated directly from the calibration function.

To obtain an independent calibration function for the particular Spectronic 20 spectrophotometer being employed in this study, an approximately 0.1 N sodium thiosulfate (Mallinckrodt No. 8100 Analytical reagent grade) solution was prepared and standardized (21) by titrating accurately weighed amounts of primary standard grade potassium dichromate (Mallinckrodt No. 6772). The standard sodium thiosulfate (0.095 N) was then used to standardize (21) an iodine solution prepared from USP grade KI (Mallinckrodt No. 1112) and analytical reagent grade iodine crystals (Mallinckrodt No. 1008). An aliquot of the standardized iodine solution (0.049 N) was diluted with ARB 2% NBKI to arrive at a working standard whose concentration was equivalent to 1 μ l of O₃ per ml (6). A series of aliquots of the working standard was further diluted with ARB 2% NBKI, and their absorbances were read on the Spectronic 20 at 350 nm. The data obtained were in excellent agreement with those furnished by the ARB.

Results and Discussion

Quantitative infrared data obtained in two separate experiments in an initial study are summarized in Table I. The ozone concentrations were calculated from the experimentally determined absorbances ($\log_{10} I_0/I$) and from the absorptivity $4.23 \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1} \text{ RTP}$.

To take advantage of the fact that several infrared spectra could be recorded during the time required to obtain the KI impinger samples and to directly compare IR and KI deter-

Table I. Ozone Concentrations Measured Simultaneously by Long-Path Infrared Spectroscopy and 2% Neutral Buffered Potassium Iodide at Ambient Conditions of Temperature, Pressure, and Concentration^a

| IR time ^b | Arbitrary units | | Absorbance | Ozone from LPIR, ^c ppm | KI time ^d | Corr ozone from LPIR, ^e ppm | Av ozone from LPIR, ppm | Ozone from 2% neutral buffered potassium iodide, ppm |
|----------------------|-----------------------|----------|------------|-----------------------------------|----------------------|--|-------------------------|--|
| | <i>I</i> ₀ | <i>I</i> | | | | | | |
| Experiment A | | | | | | | | |
| 15:16 | 76.2 | 71.2 | 0.0295 | 1.00 | | 0.99 | | |
| 15:28 | 76.31 | 71.02 | 0.0312 | 1.06 | 15:32 | 1.06 | 1.02 | 1.18 |
| 15:41 | 75.75 | 70.83 | 0.0292 | 0.99 | | 1.00 | | |
| 16:35 | 75.50 | 71.87 | 0.0214 | 0.728 | 16:24 | 0.734 | 0.734 | 0.829 |
| 17:01 | 76.48 | 73.49 | 0.0173 | 0.589 | 17:11 | 0.584 | 0.596 | 0.620 |
| 17:20 | 76.38 | 73.30 | 0.0178 | 0.604 | | 0.608 | | |
| 17:54 | 76.38 | 74.46 | 0.0111 | 0.376 | | 0.372 | | |
| 18:05 | 76.49 | 74.55 | 0.0112 | 0.379 | 18:05 | 0.379 | 0.380 | 0.431 |
| 18:18 | 76.40 | 74.43 | 0.0113 | 0.385 | | 0.390 | | |
| 19:08 | 76.12 | 75.19 | 0.00534 | 0.181 | | 0.179 | | |
| 19:22 | 76.06 | 75.28 | 0.00448 | 0.152 | 19:26 | 0.151 | 0.165 | 0.168 |
| Experiment B | | | | | | | | |
| 12:37 | 76.0 | 73.2 | 0.0163 | 0.554 | 12:53 | 0.547 | 0.544 | 0.595 |
| 12:48 | 76.0 | 73.26 | 0.0159 | 0.542 | | 0.540 | | |
| 13:16 | 75.74 | 73.12 | 0.0153 | 0.520 | 13:24 | 0.516 | 0.502 | 0.546 |
| 13:28 | 75.80 | 73.35 | 0.0143 | 0.485 | | 0.487 | | |
| 14:03 | 76.40 | 74.40 | 0.0115 | 0.392 | | 0.388 | 0.386 | 0.444 |
| 14:17 | 76.46 | 74.50 | 0.0113 | 0.384 | 14:15 | 0.385 | | |
| 15:26 | 75.77 | 74.47 | 0.00752 | 0.256 | 15:08 | 0.259 | 0.259 | 0.299 |
| 15:39 | 76.16 | 75.00 | 0.00667 | 0.226 | 15:38 | 0.226 | 0.226 | 0.284 |
| 16:13 | 75.99 | 74.79 | 0.00691 | 0.235 | 16:14 | 0.235 | 0.235 | 0.282 |
| 17:06 | 75.85 | 75.39 | 0.00264 | 0.090 | 16:59 | 0.091 | 0.091 | 0.108 |

^a During these measurements, the temperature of the samples ranged from 23.2 to 25.5 °C, the pressure ranged from 732.6 to 733.4 torr, and the relative humidity ranged from 23 to 6%. ^b Time at which scan reached 9.48 μ . ^c Based on absorptivity of $4.23 \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1} \text{ RTP}$ from ref. 19 and pathlength of 69.2 m. ^d Time halfway through 2% neutral buffered KI impinger sample. ^e $(O_3)_t(KI) = (O_3)_t(IR) e^{-k(t(KI) - t(IR))}$; $k = 8.0 \times 10^{-4} \text{ min}^{-1}$. Under these conditions, the difference between the average concentration for a 24-min sample and the ozone concentration 12 min into the sample period (i.e., at $t(KI)$) was 1 part in 10^5 of the ozone concentration; hence, the average concentration from an impinger sample was taken to be identical to the ozone concentration at $t(KI)$.

minations, the IR ozone concentrations (Column 2, Table I) were corrected to the time halfway through the corresponding KI sample. The corrections were made according to the first order function:

$$[O_3]_{t_{KI}} = [O_3]_{t_{IR}} e^{-k(t_{KI} - t_{IR})} \quad (1)$$

where t_{KI} was the time halfway through the impinger sample, t_{IR} was the time at which an infrared scan reached 9.48μ , and k ($= 8.0 \times 10^{-4} \text{ min}^{-1}$) was the average first order rate of loss of ozone (due to sampling and wall decomposition) observed during eight different sample periods using a continuous ozone analyzer (Dasibi Model 1003). The normalization of the IR ozone concentrations to the impinger half time involved corrections of less than 8 parts per billion (ppb) of ozone, except for the highest concentration (1.2 ppm) for which the correction was 10 ppb.

The normalized IR ozone concentrations for each impinger sample were averaged, and the final two columns of Table I were compared to the corresponding KI ozone concentrations. The latter were obtained from measured absorbances for impinger samples and a linear regression fit to the ARB calibration data

$$\text{Ozone} = 1.0095 (\text{Absorbance}) - 0.0015 \quad (2)$$

Calibration data obtained in our laboratory using USP grade KI yielded a function ($\text{Ozone} = 0.987 \text{ Absorbance} + 0.0014$) which was in excellent agreement (2%) with the ARB data. Earlier calibration data obtained in our laboratory using reagent grade KI yielded ozone concentrations lower by approximately 5%. We subsequently learned (22, 23) that reagent grade KI often contains a reducing agent to prevent the oxidation of iodide to iodine during shelf life, whereas KI meeting USP specifications usually contains little or no reducing agent.

The KI and IR data from Table I are plotted in Figure 5. The linear regression equation for these data for an unrestricted intercept is

$$[O_3]^{KI} = 1.12 [O_3]^{IR} + 0.001 \quad (3)$$

where ozone concentrations are in parts per million, and the standard deviations for the slope and intercept are ± 0.03 and ± 0.014 , respectively. Thus, results from this experiment suggested that the ARB 2% NBKI method yielded ozone concentrations some 12% higher than concentrations obtained from absolute infrared measurements.

Humidity Effect. During the course of these experiments, the humidity ranged from $\sim 20\%$ down to $\sim 10\%$ as the ozone sample was diluted by flushing the chamber with essentially dry air. (It was not believed important at the time of these experiments to hold the RH rigorously constant.) However, a commercial UV analyzer (Dasibi Model 1003) was being used as a convenient continuous, "real time" monitor of the relative ozone concentration in the chamber, and it was observed that whereas the ratio of KI to IR concentrations was ~ 1.1 , the ratio of Dasibi to IR concentrations was approximately 1.2 although the Dasibi itself was calibrated by the ARB 2% NBKI method and therefore should have yielded concentrations in the same ratio to the IR measurements.

It was first demonstrated that the difference observed between the Dasibi and 2% NBKI measurements was not due to the fact that the chamber experiments represented a static sampling condition, whereas the normal 2% NBKI calibration procedure is conducted using a dynamic flow system. The only other obvious difference in procedure appeared to be the fact that the ARB calibration procedure is normally conducted at ambient relative humidities (which typically might range from 40–60%), whereas the chamber experiment was carried out at an average relative humidity of approximately 18%. To investigate the possible dependence of the 2% NBKI method

on relative humidity, a comparison of ozone concentrations measured simultaneously by IR and 2% NBKI was made as described above but with the relative humidity in the chamber held at 50% throughout the experiment. Data obtained in this experiment were not corrected for the very slow ozone decay in the chamber or for the small sampling losses since from the previous analysis, it was clear that these corrections (typically less than 5 ppb) were negligible compared to random variations in the KI bubbler measurements (see Table I).

The data obtained are shown in Table II and plotted in Figure 6. Linear regression analyses of these data yielded the functions

$$[O_3]^{NBKI} = (1.23 \pm 0.06)[O_3]^{IR} + (0.001 \pm 0.034) \quad (4)$$

$$[O_3]^{DSBI} = (1.22 \pm 0.05)[O_3]^{IR} - (0.030 \pm 0.027) \quad (5)$$

$$[O_3]^{DSBI} = (0.99 \pm 0.04)[O_3]^{NBKI} - (0.028 \pm 0.027) \quad (6)$$

Thus, for 50% relative humidity the Dasibi (DSBI) and 2% NBKI data are in good agreement as expected, but both are some 23% higher than the concentrations measured by the infrared method. These results strongly suggest that the response obtained by the 2% NBKI method is dependent upon the relative humidity of the ozone sample stream, although we are unaware of any obvious chemical interpretation for this effect since the reaction that is presumed to hold (6)

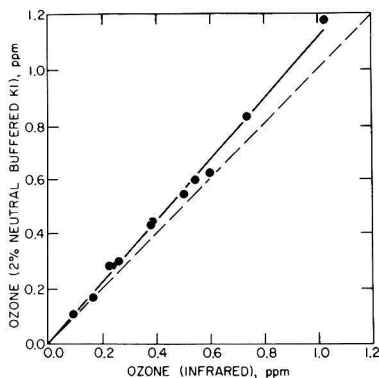
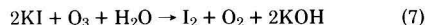


Figure 5. Linear regression fit of ozone concentrations measured by LPIR and 2% NBKI methods at an average relative humidity of 18%; slope = 1.12 ± 0.03 , intercept = 0.001 ± 0.014

Table II. Ozone Concentrations Measured Simultaneously at 50% Relative Humidity by Long-Path Infrared Spectroscopy, 2% Neutral Buffered Potassium Iodide, and Dasibi UV Ozone Analyzer Calibrated Against 2% NBKI^a

| Ozone from LPIR, ^b ppm | Ozone from 2% NBKI, ppm | Ozone from Dasibi calibrated against 2% NBKI, ^c ppm |
|--------------------------------------|----------------------------|--|
| 0.655 | 0.792 | 0.787 |
| 0.648 | 0.834 | 0.772 |
| 0.651 | 0.790 | 0.751 |
| 0.509 | 0.623 | 0.595 |
| 0.524 | 0.638 | 0.585 |
| 0.348 | 0.463 | 0.422 |
| 0.241 | 0.279 | 0.252 |

^a Sample temperature and pressure were 24.3 °C and 736 torr, respectively. ^b Based on absorptivity of $4.23 \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1}$ RTP from ref. 19 and pathlength of 69.2 m. ^c Calibrated at ambient relative humidity.

takes place in an aqueous solution. Following completion of the present study, an extensive joint investigation of humidity effects by the LAAPCD, ARB, and EPA (Region IX) yielded data for the 2% NBKI method and Dasibi ozone analyzers which are consistent with the data reported here (24).

Comparison with Ultraviolet Measurements. An additional significant study in this investigation was a collaborative effort with W. B. DeMore (25) who participated in an experiment similar to those described above. In this study, conducted for ozone samples in dry matrix air (RH ~3%) in the evacuable chamber, DeMore recorded data with a Dasibi ozone analyzer which he had previously calibrated against a 1-m UV photometer. Simultaneously, ozone concentrations were also measured using the in-situ long-path infrared spectrophotometer, 2% NBKI impingers, and two Statewide Air Pollution Research Center (SAPRC) Dasibi instruments previously calibrated against the 2% NBKI method at ambient relative humidity. The data obtained in this study are summarized in Table III, and appropriate linear regression equations for the various sets of measurements are as follows:

$$[\text{O}_3]^{\text{UV}} = (0.99 \pm 0.02)[\text{O}_3]^{\text{IR}} + (0.016 \pm 0.011) \quad (8)$$

$$[\text{O}_3]^{\text{NBKI}} = (1.14 \pm 0.04)[\text{O}_3]^{\text{IR}} + (0.013 \pm 0.023) \quad (9)$$

$$[\text{O}_3]^{\text{NBKI}} = (1.16 \pm 0.02)[\text{O}_3]^{\text{UV}} - (0.007 \pm 0.012) \quad (10)$$

$$[\text{O}_3]^{\text{DSBI} \#1} = (1.25 \pm 0.03)[\text{O}_3]^{\text{IR}} + (0.012 \pm 0.017) \quad (11)$$

$$[\text{O}_3]^{\text{DSBI} \#2} = (1.24 \pm 0.03)[\text{O}_3]^{\text{IR}} + (0.007 \pm 0.017) \quad (12)$$

Equation 8 shows that the UV measurements made by DeMore using a Dasibi instrument as a transfer standard, and

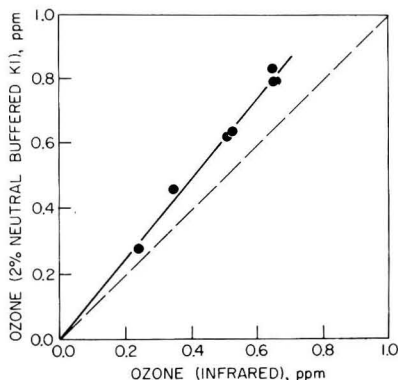


Figure 6. Linear regression fit of ozone concentrations measured by LPIR and 2% NBKI methods at a relative humidity of ~50%; slope = 1.23 ± 0.06 , intercept = 0.001 ± 0.034

based on an ultraviolet absorptivity of $135 \text{ cm}^{-1} \text{ atm}^{-1}$ at 253.7 nm, were in excellent agreement with simultaneous in-situ long-path infrared measurements based on an infrared absorptivity of $4.23 \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1}$ RTP. Thus, the two spectroscopic methods gave comparable results (as shown in Equations 9 and 10) for comparison with the 2% NBKI measurements. Specifically, for the dry sample stream provided in this experiment, the ARB 2% NBKI method yielded ozone values some 14–16% higher than either the UV or IR measurements.

However, as seen from Equations 11 and 12, the two SAPRC Dasibi instruments which had been previously calibrated by the ARB 2% NBKI method at ambient relative humidities, and which have been shown (24) to respond essentially independently of the RH of ozone sample streams, gave ozone values some 25% higher than those obtained by the IR (or UV) measurements. The independence of the Dasibi data with respect to the relative humidity of the sample stream is illustrated by the agreement between Equations 11 and 5 obtained for relative humidities of 3% and 50%, respectively.

Comparison with a Previous Infrared Study. In the only previously published report (11) of an investigation of the neutral buffered potassium iodide method by long-path infrared spectroscopy, Kopczynski and Bufalini described a study of the 1% NBKI method over a range of ozone concentrations from 2 to 20 ppm, apparently for dry air. For an unrestricted intercept they obtained regression Equation 13

$$[\text{O}_3]^{\text{NBKI}} = 0.947[\text{O}_3]^{\text{IR}} - 0.22 \quad (13)$$

with a standard error estimate, S_y , of ± 0.28 ppm. When the intercept was restricted to zero, their data fit Equation 14

$$[\text{O}_3]^{\text{NBKI}} = 0.929[\text{O}_3]^{\text{IR}} \quad (14)$$

with a standard error, S_y , of ± 0.32 ppm.

The slopes of 0.95 and 0.93 in these equations may be contrasted with those of 1.14 and 1.23 observed in the present study for the 2% NBKI method for 3% and 50% RH, respectively. Kopczynski and Bufalini concluded from their results that 1:1 stoichiometry is valid for the 1% NBKI method within their experimental error. However, in view of the recently demonstrated effects on KI measurements due to humidity, the nature of potassium iodide reagent employed, etc., and since Kopczynski and Bufalini worked at ozone concentrations from 2 to 20 ppm with a resulting large intercept for extrapolation of their data to the ambient concentration range, the 10–25% deviation from unit stoichiometry observed in this and other recent investigations could well have been masked in their earlier study. Thus, although different conclusions were reached in the previous (11) and present infrared studies concerning the stoichiometry of the NBKI methods, there is no inherent conflict in the data obtained in these investigations.

Table III. Ozone Concentrations Measured Simultaneously at ~3% Relative Humidity by LPIR, 2% NBKI, and Dasibi Ozone Analyzers Calibrated by UV Photometry and 2% NBKI, Respectively^a

| Ozone from LPIR, ^b ppm | Ozone from Dasibi calibrated against UV photometry, ^c ppm | Ozone from 2% NBKI, ppm | Ozone from Dasibi calibrated against 2% NBKI, ^d ppm | |
|--------------------------------------|--|-------------------------|---|-----------|
| | | | Dasibi #1 | Dasibi #2 |
| 0.780 | 0.776 | 0.884 | 0.973 | 0.961 |
| 0.627 | 0.638 | 0.736 | 0.798 | 0.796 |
| 0.450 | 0.468 | 0.551 | 0.588 | 0.580 |
| 0.328 | 0.347 | 0.391 | 0.432 | 0.420 |
| 0.161 | 0.164 | 0.178 | 0.196 | 0.193 |

^a Sample temperature and pressure were 23.9 °C and 735 torr, respectively. ^b Based on absorptivity of $4.23 \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1}$ RTP from ref. 19 and pathlength of 69.2 m. ^c Instrument calibrated and employed by W. B. DeMore. ^d Calibrated at ambient relative humidity.

Conclusions

Results obtained in this study indicate that rather than being unity, as had been thought prior to 1974, the stoichiometry of the 2% NBKI ozone (or oxidant) analyzer calibration procedure employed by the California Air Resources Board from 1960 until June 1, 1974, ranges from ~1.12 to ~1.25, depending upon whether the relative humidity of the sample stream is low or high, respectively. The results obtained at low humidities may also be relevant to the 1% NBKI calibration procedure specified in the *Federal Register* (5) in view of the near equivalence (to within ~5%) of the ARB 2% NBKI method and EPA 1% NBKI method demonstrated by most (26–29), although not all (30) previous comparisons of the two methods. Further investigation of the 1% NBKI *Federal Register* method and development of a replacement for this calibration procedure are currently being carried out by the EPA (31). Effective June 1, 1975, the California calibration procedure for oxidant (ozone) was changed from the 2% neutral buffered potassium iodide method to an ultraviolet photometry method employing a 1-m UV photometer as a primary standard and a Dasibi UV ozone analyzer as a portable secondary standard for field calibrations (32).

Within experimental uncertainties encountered in the use of the potassium iodide methods by different laboratories, the data obtained for comparison with long-path infrared measurements are consistent with data obtained for comparison of the NBKI methods with UV photometry [in our laboratory, as reported here, and in other more extensive studies (28, 29, 33, 34)] and with recent data reported for comparison with gas-phase titration (GPT) measurements (33). It thus appears that IR, UV, and GPT measurement methods for ozone have been reconciled and, when carefully carried out, that each can be relied upon to provide absolute ozone concentrations against which ambient air analyzers can be calibrated, either directly or by means of "transfer" standards. Uniform adoption of one or more of these methods by local, state, and federal agencies and abandonment of the wet chemical potassium iodide methods seem necessary and desirable if an accurate, reliable, and common data base of ozone measurements is to be achieved.

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Corrected South Coast Air Basin Oxidant Data: Some Conclusions and Implications

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■ The rationale for and the results obtained by scaling existing oxidant air quality data for Los Angeles County (LAC) air monitoring stations by a factor of 1.1 and existing air quality data for non-LAC stations by a factor of 0.8 are presented. Thus, an internally consistent set of oxidant data for the California South Coast Air Basin is generated. The scaled oxidant data show that, contrary to the indications of the data as reported, cities such as Azusa and Pasadena in LAC have higher yearly total oxidant levels than cities in the easternmost portion of the Basin. The scaled data also show that non-LAC oxidant dosages are substantially lower than was previously believed. Furthermore, if non-LAC oxidant data and any oxidant episode levels dependent on data referenced to neutral buffered KI are both scaled downward by 0.8, the new dosage calculated using the scaled standard and scaled data is lower than the old dosage by 20%.

The Federal Air Quality Standard for oxidant (1), many health alert levels and control programs for oxidant, and models of oxidant formation and transport are based substantially on air monitoring data from the Los Angeles basin, which is the most densely populated portion of the California South Coast Air Basin (Figure 1). The South Coast Air Basin actually encompasses all of Orange and Ventura counties and portions of Los Angeles, Riverside, San Bernardino, and Santa Barbara counties. Figure 1 shows that portion of the South Coast Air Basin which surrounds metropolitan Los Angeles and lies below the 1500-ft contour of the mountains that define the Los Angeles basin. Currently, some 10 million people live in the South Coast Air Basin.

In June 1974 the California Air Resources Board (ARB) and the Los Angeles County Air Pollution Control District (LAAPCD) announced jointly that different methods of calibration of oxidant monitoring instruments caused oxidant measurements made by the LAAPCD to be "one-quarter to one-third" lower than ARB measurements made at the same time and place (2). This significant measurement disparity was first observed more than a year earlier, during the late spring and early summer of 1973, when the ARB operated a mobile air monitoring van—first, near the Pomona air monitoring station of the LAAPCD and, second, adjacent to the LAAPCD station in Azusa. Oxidant measurements recorded in the ARB van were 20–40% above those recorded by the Pomona LAAPCD station and about 30% higher than those recorded by the Azusa LAAPCD station (3). Since the sampling techniques and instruments used were similar, it was suspected that the measurement discrepancy resulted from differences in the methods used to calibrate the analyzers. Accordingly, the California Air and Industrial Hygiene Laboratory (AIHL) and the ARB performed a laboratory study using ozone, which showed that the methods used by the ARB and the Environmental Protection Agency (EPA) to calibrate their oxidant analyzers were equivalent within experimental error under the conditions of the study, but that the method used by the LAAPCD to calibrate its oxidant analyzers yielded readings 69–73% as high as those obtained by the ARB calibration method (3, 4).

Until June 1, 1975, all three agencies (ARB, EPA, and LAAPCD) used the oxidation by ozone of aqueous iodide ion

to molecular iodine as the basis for their calibration methods. The ARB (5) used a 2% neutral buffered potassium iodide absorbing solution and determined the released molecular iodine spectrophotometrically. The spectrophotometer was calibrated against iodine solutions which had been standardized by titration with $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$. The $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ was standardized against primary grade $\text{KH}(\text{IO}_3)_2$. The EPA calibration procedure (6) was similar to that formerly used by the ARB, except that essentially dry air and 1% neutral buffered KI were used, and the spectrophotometer was calibrated using I_2 solutions standardized against primary grade As_2O_3 . The LAAPCD (7) used 2% neutral unbuffered KI, and the released I_2 was titrated using 0.002 N $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ which had been standardized against $\text{K}_2\text{Cr}_2\text{O}_7$.

Because the LAAPCD calibration method is difficult to perform (4), to confirm the AIHL/ARB results:

"... a joint ARB-LAAPCD study was conducted at the laboratories of the LAAPCD. Two colorimetric oxidant analyzers, one provided by the ARB and one by the LAAPCD, were used to sample simultaneously from a common manifold. The ozone concentration in the manifold was determined by the three [EPA, ARB, LAAPCD] calibration methods. Again it was demonstrated that the EPA and ARB procedures were approximately equivalent, while, on the average, concentrations by the LAAPCD method were approximately 70% of those by the ARB method." (3)

Because of the discrepancy between LAAPCD oxidant measurements and non-Los Angeles County oxidant measurements, on August 15, 1974, the ARB appointed an ad hoc committee to evaluate oxidant calibration methods. The ad hoc committee (8) used a UV photometer ($[\text{O}_3]_{\text{absolute}}^{\text{UV}}$) to calibrate the response to ozone of a Dasibi ozone monitor ($[\text{O}_3]_{\text{Dasibi}}$). The Dasibi was then used to determine the response of the LAAPCD, ARB, and EPA iodimetric calibration methods ($[\text{O}_3]_{\text{LAAPCD}}$, $[\text{O}_3]_{\text{ARB}}$, $[\text{O}_3]_{\text{EPA}}$). The latter measurements were made simultaneously at about 50% relative humidity. Analysis of the resulting data yielded the following regression lines (8):

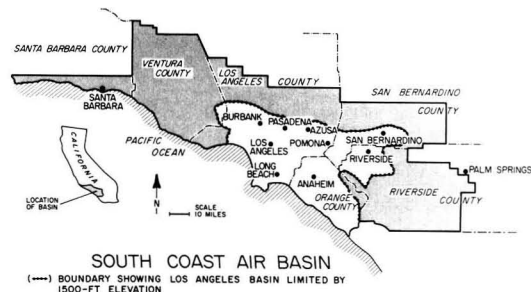


Figure 1. Map of South Coast Air Basin (outer limits shaded gray) showing extent of Los Angeles Basin (white region), as defined by 1500-ft contour of surrounding mountains. Locations of nine air monitoring stations in Los Angeles Basin from which data are used in this paper are indicated on map

$$[\text{O}_3]_{\text{absolute}}^{\text{UV}} = 1.054[\text{O}_3]_{\text{Dasibi}} + 0.028 \quad (1)$$

$$[\text{O}_3]_{\text{ARB}} = 1.29[\text{O}_3]_{\text{Dasibi}} - 0.005 \quad (2)$$

$$[\text{O}_3]_{\text{LAAPCD}} = 0.96[\text{O}_3]_{\text{Dasibi}} - 0.032 \quad (3)$$

$$[\text{O}_3]_{\text{EPA}} = 1.24[\text{O}_3]_{\text{Dasibi}} - 0.035 \quad (4)$$

However, the responses of all of the iodometric methods are humidity dependent (9), whereas the response to ozone of Dasibi ozone monitors is not dependent on humidity. This humidity effect was studied by a joint ARB-LAAPCD-EPA team (10, 11). The EPA calibration procedure (6) employs essentially dry air. The response of the various iodometric methods was determined at 0, 20, 40, and 60% relative humidity (RH) compared to that of a Dasibi which had been calibrated by the ARB 2% neutral buffered KI method. Because field ozone monitors are calibrated by spanning them against iodometric measurements, the study team concluded in their draft report (10) that regression lines forced through zero best approximated actual calibration procedures for field instruments. The slopes of the regression lines forced through zero given in the final report of the ARB-LAAPCD-EPA humidity study (11) may be used to formulate an equation which gives the variation with relative humidity of the relative response of the ARB and LAAPCD iodometric calibration methods:

$$[\text{O}_3]_{\text{ARB}}/[\text{O}_3]_{\text{LAAPCD}} = 3.56 \times 10^{-3} \text{RH} + 1.28 \quad (5)$$

At 50% RH this equation gives a value of $[\text{O}_3]_{\text{ARB}}/[\text{O}_3]_{\text{LAAPCD}} = 1.46$. Significantly, if the data of the ad hoc committee (8) are also forced to zero, then at RH ~50% a value of $[\text{O}_3]_{\text{ARB}}/[\text{O}_3]_{\text{LAAPCD}} = 1.43$ is obtained. Previous studies of ozonized room air obtained the following values for this ratio: 1.37, 1.43, and 1.46 by Tang et al. (4); 1.34 by Crowe (12); and 1.33 and 1.39 by Holland (13). A value of 1.37 was obtained by Dickinson (14) for the ratio of the LAAPCD iodometric calibration procedure when run with and without buffering at pH 7. The average of these values is $[\text{O}_3]_{\text{ARB}}/[\text{O}_3]_{\text{LAAPCD}} = 1.40 \pm 0.05$. Significantly, after an independent assessment of the available data (10), the ARB also concluded that $[\text{O}_3]_{\text{ARB}}/[\text{O}_3]_{\text{LAAPCD}} = 1.4$.

An investigation of the validity of the ARB calibration technique was performed at the Statewide Air Pollution Research Center (SAPRC) (15) and showed that at 50% RH, $[\text{O}_3]_{\text{absolute}}^{\text{IR}}/[\text{O}_3]_{\text{ARB}} = 0.81$, which is in good agreement with the value of $[\text{O}_3]_{\text{absolute}}^{\text{UV}}/[\text{O}_3]_{\text{ARB}} = 0.78$ obtained by the ad hoc committee using UV photometry. Taken together, these two values suggest that ambient oxidant data referenced to the ARB 2% neutral buffered KI method be corrected using the following equation:

$$[\text{O}_3]_{\text{absolute}} = 0.8[\text{O}_3]_{\text{ARB}} \quad (6)$$

Again, this conclusion is in exact agreement with a previous ARB recommendation (16). Further, if $[\text{O}_3]_{\text{ARB}}/[\text{O}_3]_{\text{LAAPCD}} = 1.4$, then the following equation should be used to correct ambient oxidant data referenced to the LAAPCD 2% neutral unbuffered method:

$$[\text{O}_3]_{\text{absolute}} = 1.1[\text{O}_3]_{\text{LAAPCD}} \quad (7)$$

Calculations

We have used Equations 6 and 7 and a computer (IBM 360/50) to generate an internally consistent set of ambient oxidant data for 18 air monitoring stations located in the South Coast Air Basin. Hourly average oxidant data as reported for the years 1955 through 1974 were obtained from the ARB and the LAAPCD stored on magnetic tapes. Hourly average oxidant data from air monitoring stations in Los Angeles County are available on tapes from the LAAPCD. Under contract to the ARB, hourly average oxidant mea-

surements are made by non-Los Angeles stations. These measurements comprise the data base stored on tapes by the ARB.

The computer program used surveyed the data available one day at a time, dropping days for which three or more consecutive daytime hours of data were lacking. When one or two consecutive hours of data were lacking, a four-point Lagrangian interpolation was used to estimate the missing data points. The resulting set of internally consistent (hereinafter termed "corrected") oxidant data is probably accurate to about $\pm 10\%$.

Results

For the full 19-year period from 1955 through 1974, complete data are not available for any of the 18 stations surveyed. When data are available for a specified station and year, they are not available for all 365 days of that year. Further, because the days for which data are lacking are not distributed throughout the year in a strictly random fashion, no normalization to 365 days was possible. Therefore, all yearly totals reported here (Tables I-III) are minimum values. Conversely, because the missing days are not bunched either during the smog season or during the winter, the data also do not contain any significant intrinsic biases.

Because the South Coast Air Basin oxidant data are voluminous, we have chosen to present here only data for the years 1973 and 1974 and for the following nine air monitoring stations: Long Beach, Los Angeles downtown, Burbank, Pasadena, Azusa, and Pomona (all in Los Angeles County); Anaheim (Orange County); Riverside (Riverside County); and San Bernardino (San Bernardino County). Figure 1 shows the locations of the nine air monitoring stations from which the data used in this study were taken. As was stated above, the Los Angeles County stations used oxidant analyzers calibrated by the LAAPCD method (7), whereas the non-Los Angeles County stations used analyzers calibrated by the ARB method (5). Data from other stations and for other years will be published as a SAPRC report (17).

To facilitate discussion of the implications of the corrected data presented in Tables I-III, we have summarized the corrected hourly average values of oxidant in terms of the number of days per year, the number of hours per year, and the yearly dosage (hours \times concentration) for which the following levels of oxidant were equaled or exceeded: 0.08, 0.20, and 0.35 ppm. These levels were chosen because 0.08 ppm for 1 h is the Federal Air Quality Standard for oxidant, and 0.20 and 0.35 ppm for 1 h are the California first and second episode criteria levels for oxidant (18). Reference will also be made to the California third stage episode criteria level (0.50 ppm for 1 h and predicted to persist for an additional hour) for oxidant (18) and to the federal "significant harm" level (0.60 ppm) for oxidant (19).

On May 15, 1975, the California Air Resources Board adopted UV photometric measurement of ozone as the state reference method for the calibration of oxidant monitors (20). On the same day, the ARB changed the state's second and third episode criteria levels for oxidant from 0.40 and 0.60 ppm to 0.35 and 0.50 ppm (18). Changes were made because, "The [old] stage 2 and stage 3 levels . . . [were] based predominantly on experimental exposures of human subjects to ozone, calibrated using neutral buffered potassium iodide reagent" (21). Accordingly, since the neutral buffered potassium iodide calibration procedure for ozone yields readings high about 25%, the ARB chose to reduce the old stage 2 and stage 3 episode criteria levels so that they will be in better conformity with ambient oxidant measurements referenced to UV photometric measurements of ozone.

Oxidant Transport. For many years, the air monitoring data—as reported by the LAAPCD and the APCD's of Riv-

erside, San Bernardino, and Orange counties—have shown that the highest oxidant levels in the South Coast Air Basin occur at cities such as Riverside and San Bernardino, which lie in the less-populated eastern portion of the basin. The conventional explanation (22, 23) for this seeming anomaly

has generally been the following: Large amounts of hydrocarbons and oxides of nitrogen are emitted during the morning traffic rush hour, principally in the more densely populated western regions of the basin. While being transported toward the eastern portion of the basin by the prevailing onshore sea

Table I. Days for which Oxidant $\geq 0.08, 0.20,$ and 0.35 ppm^a

| 1973 | | | | | | | | | |
|-----------------|-----|------|-----|-----|-----|-----|------|------|------|
| Station | LB | LADT | Bur | Pas | Azu | Pom | SB | Riv | Ana |
| Total days | 347 | 349 | 353 | 350 | 346 | 351 | 322 | 355 | 344 |
| ≥ 0.08 ppm | | | | | | | | | |
| As reported | 17 | 134 | 159 | 183 | 184 | 174 | 169 | 195 | 105 |
| Corrected | 34 | 160 | 171 | 194 | 194 | 189 | 154 | 172 | 72 |
| Ratio | 2.0 | 1.2 | 1.1 | 1.1 | 1.1 | 1.1 | 0.91 | 0.88 | 0.69 |
| ≥ 0.20 ppm | | | | | | | | | |
| As reported | 2 | 11 | 12 | 53 | 61 | 40 | 80 | 71 | 15 |
| Corrected | 2 | 15 | 19 | 68 | 82 | 52 | 33 | 46 | 7 |
| Ratio | 1.0 | 1.4 | 1.6 | 1.3 | 1.3 | 1.3 | 0.41 | 0.65 | 0.47 |
| ≥ 0.35 ppm | | | | | | | | | |
| As reported | 0 | 1 | 0 | 4 | 6 | 0 | 5 | 4 | 0 |
| Corrected | 0 | 2 | 0 | 6 | 9 | 2 | 0 | 0 | 0 |
| 1974 | | | | | | | | | |
| Station | LB | LADT | Bur | Pas | Azu | Pom | SB | Riv | Ana |
| Total days | 350 | 333 | 360 | 351 | 360 | 360 | 360 | 356 | 335 |
| ≥ 0.08 ppm | | | | | | | | | |
| As reported | 27 | 156 | 190 | 228 | 220 | 178 | 195 | 208 | 101 |
| Corrected | 37 | 175 | 207 | 243 | 233 | 194 | 172 | 184 | 60 |
| Ratio | 1.4 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 0.88 | 0.89 | 0.59 |
| ≥ 0.20 ppm | | | | | | | | | |
| As reported | 0 | 14 | 30 | 52 | 80 | 49 | 95 | 94 | 4 |
| Corrected | 0 | 30 | 48 | 80 | 99 | 72 | 73 | 65 | 2 |
| Ratio | ... | 2.1 | 1.6 | 1.5 | 1.2 | 1.5 | 0.77 | 0.69 | 0.50 |
| ≥ 0.35 ppm | | | | | | | | | |
| As reported | 0 | 0 | 1 | 0 | 2 | 0 | 25 | 8 | 0 |
| Corrected | 0 | 0 | 1 | 2 | 6 | 0 | 1 | 0 | 0 |

^a LB = Long Beach, LADT = Los Angeles downtown, Bur = Burbank, Pas = Pasadena, Azu = Azusa, Pom = Pomona, SB = San Bernardino, Riv = Riverside, and Ana = Anaheim. Corrected data means LAAPCD data x 1.1 and ARB data x 0.8. Ratio = Corrected/As reported.

Table II. Hours for which Oxidant $\geq 0.08, 0.20,$ and 0.35 ppm^a

| 1973 | | | | | | | | | |
|-----------------|-----|------|------|------|------|------|------|------|------|
| Station | LB | LADT | Bur | Pas | Azu | Pom | SB | Riv | Ana |
| Total days | 347 | 349 | 353 | 350 | 346 | 351 | 322 | 355 | 344 |
| ≥ 0.08 ppm | | | | | | | | | |
| As reported | 46 | 615 | 745 | 1122 | 1129 | 936 | 1182 | 1363 | 389 |
| Corrected | 85 | 777 | 894 | 1282 | 1267 | 1088 | 962 | 1101 | 213 |
| Ratio | 1.8 | 1.3 | 1.2 | 1.1 | 1.1 | 1.2 | 0.81 | 0.81 | 0.55 |
| ≥ 0.20 ppm | | | | | | | | | |
| As reported | 2 | 38 | 25 | 147 | 189 | 105 | 244 | 264 | 31 |
| Corrected | 4 | 51 | 46 | 217 | 264 | 150 | 88 | 109 | 13 |
| Ratio | 2.0 | 1.3 | 1.8 | 1.5 | 1.4 | 1.4 | 0.36 | 0.41 | 0.42 |
| ≥ 0.35 ppm | | | | | | | | | |
| As reported | 0 | 5 | 0 | 7 | 10 | 0 | 5 | 7 | 0 |
| Corrected | 0 | 6 | 0 | 11 | 15 | 2 | 0 | 0 | 0 |
| 1974 | | | | | | | | | |
| Station | LB | LADT | Bur | Pas | Azu | Pom | SB | Riv | Ana |
| Total days | 350 | 333 | 360 | 351 | 360 | 360 | 360 | 356 | 335 |
| ≥ 0.08 ppm | | | | | | | | | |
| As reported | 53 | 773 | 995 | 1246 | 1280 | 963 | 1414 | 1504 | 372 |
| Corrected | 83 | 983 | 1186 | 1446 | 1490 | 1136 | 1150 | 1205 | 214 |
| Ratio | 1.6 | 1.3 | 1.2 | 1.2 | 1.2 | 1.2 | 0.81 | 0.80 | 0.58 |
| ≥ 0.20 ppm | | | | | | | | | |
| As reported | 0 | 25 | 72 | 131 | 222 | 120 | 401 | 333 | 11 |
| Corrected | 0 | 59 | 115 | 210 | 306 | 197 | 217 | 171 | 5 |
| Ratio | ... | 2.4 | 1.6 | 1.6 | 1.4 | 1.6 | 0.54 | 0.51 | 0.45 |
| ≥ 0.35 ppm | | | | | | | | | |
| As reported | 0 | 0 | 1 | 0 | 3 | 0 | 36 | 9 | 0 |
| Corrected | 0 | 0 | 2 | 3 | 8 | 0 | 1 | 0 | 0 |

^a LB = Long Beach, LADT = Los Angeles downtown, Bur = Burbank, Pas = Pasadena, Azu = Azusa, Pom = Pomona, SB = San Bernardino, Riv = Riverside, and Ana = Anaheim. Corrected data means LAAPCD data x 1.1 and ARB data x 0.8. Ratio = Corrected/As reported.

breezes, the oxides of nitrogen promote the photooxidation of the hydrocarbon pollutants. Ozone, the principal component of oxidant, is a major product of this complicated process (24-28). Because it is consumed rapidly by NO to produce NO₂ and O₂, ozone does not begin to accumulate until almost all of the NO has been converted to NO₂. Because ozone formation is delayed, downwind transport causes oxidant levels in eastern cities of the basin, such as Riverside and San Bernardino, to exceed those of the more densely populated regions to their west.

This conventional view was reiterated in a recent National Academy of Sciences-National Academy of Engineering (NAS-NAE) report (29), which stated:

"Thus, over a period of hours the mass of smog-laden air from downtown Los Angeles experiences a growth in ozone concentration as it travels eastward so that a shift in maximum ozone concentrations eastward should be expected, and has been confirmed by measurements. The shift in ozone concentrations to the east also has been enhanced by the growth in urbanization in that region, which causes increases in local hydrocarbon and NO_x emissions."

One can examine the two parts of this statement separately. First, is there a downwind transport of oxidant and, second, does oxidant buildup occur during downwind transport?

On the basis of published data, the evidence for downwind transport of pollutants is convincing. For example, Figure 2 presents the diurnal variation of oxidant levels on July 25, 1973, at four air monitoring stations—Los Angeles downtown, Pomona, Riverside, and Palm Springs—which lie on a west-east axis across the South Coast Air Basin. The second late afternoon peak in the oxidant profiles at Pomona, Riverside, and Palm Springs is a common occurrence, which is best explained by windborne transport of pollutants to the inland cities from regions nearer the coast. This long-held view of

pollutant transport is supported by two recent studies. The first, a fluorescent tracer study, showed that some coastal air parcels do reach inland cities, such as Riverside and San Bernardino (30), in the span of one day. The second, analyses of observational data of air pollutants from an airborne sampling system, indicated that ozone and/or its precursors in an episode were transported in the Los Angeles basin from the metropolitan area to the eastern portion of the basin (31).

If the oxidant maxima in Figure 2 are spaced proportionately to the distances between the four cities, as has been done in the figure, the second oxidant maxima fall on the same connecting line (32). This result suggests that the average wind speed in the basin on July 25, 1973, was about 10 mph in an easterly direction. In fact, the average ground wind speed on that day actually was approximately 8 mph in an east-northeasterly direction.

The evidence for the NAS-NAE statement, "... a shift in maximum ozone concentrations eastward should be expected, and has been confirmed by measurements" (29), is typified in Figure 3a. This shows the number of days in 1973 on which the reported average hourly oxidant readings equaled or exceeded 0.20 ppm at six South Coast Air Basin air monitoring stations. Clearly, the data as reported do indeed suggest an inland buildup of oxidant. However, when all the air monitoring data are placed on a consistent scale, no matter which scale is used, the corrected data (Figure 3b-e) show that in 1973, cities such as Pasadena, Azusa, and Pomona actually had significantly higher oxidant levels than did Riverside and San Bernardino. Tables I and II show that this conclusion also holds for 1974. It is also true for all other years for which data are available (1963-1970). Clearly, oxidant levels do not increase along a west-to-east axis across the basin. However, data from other stations indicate that they do increase along a southwest-to-northeast axis across the basin, which roughly matches the orientation of the prevailing onshore sea breezes. Thus, buildup of oxidant during downwind transport may

Table III. Oxidant Dosage (ppm × h) ≥ 0.08, 0.20, and 0.35 ppm^a

| Station | 1973 | | | | | | | | | |
|-------------|-----------|------|------|------|------|------|------|------|------|--|
| | LB | LADT | Bur | Pas | Azu | Pom | SB | Riv | Ana | |
| Total days | 347 | 349 | 353 | 350 | 346 | 351 | 322 | 355 | 344 | |
| | -0.08 ppm | | | | | | | | | |
| As reported | 1.32 | 22.0 | 27.1 | 62.0 | 70.5 | 47.1 | 84.7 | 92.5 | 14.5 | |
| Corrected | 1.84 | 29.2 | 35.5 | 76.8 | 86.1 | 58.9 | 51.2 | 55.7 | 7.62 | |
| Ratio | 1.4 | 1.3 | 1.3 | 1.2 | 1.2 | 1.3 | 0.60 | 0.60 | 0.53 | |
| | -0.20 ppm | | | | | | | | | |
| As reported | 0 | 3.02 | 0.61 | 6.39 | 8.85 | 3.38 | 10.3 | 11.7 | 1.27 | |
| Corrected | 0.04 | 4.15 | 1.26 | 10.2 | 13.6 | 5.91 | 2.81 | 2.91 | 0.22 | |
| Ratio | ... | 1.4 | 2.1 | 1.6 | 1.5 | 1.7 | 0.27 | 0.25 | 0.17 | |
| | -0.35 ppm | | | | | | | | | |
| As reported | 0 | 0.54 | 0 | 0.34 | 0.38 | 0 | 0.12 | 0.12 | 0 | |
| Corrected | 0 | 0.77 | 0 | 0.64 | 0.82 | 0 | 0 | 0 | 0 | |
| Station | 1974 | | | | | | | | | |
| | LB | LADT | Bur | Pas | Azu | Pom | SB | Riv | Ana | |
| Total days | 350 | 333 | 360 | 351 | 360 | 360 | 360 | 356 | 335 | |
| | -0.08 ppm | | | | | | | | | |
| As reported | 1.24 | 28.7 | 44.7 | 61.8 | 78.4 | 52.1 | 119 | 109 | 12.1 | |
| Corrected | 1.79 | 37.5 | 56.8 | 77.6 | 96.0 | 64.8 | 75.9 | 67.1 | 5.92 | |
| Ratio | 1.4 | 1.3 | 1.3 | 1.3 | 1.2 | 1.2 | 0.64 | .62 | 0.49 | |
| | -0.20 ppm | | | | | | | | | |
| As reported | 0 | 0.31 | 1.88 | 4.04 | 7.78 | 3.83 | 24.3 | 17.8 | 0.44 | |
| Corrected | 0 | 0.99 | 3.48 | 7.22 | 13.2 | 6.81 | 8.20 | 5.24 | 0.12 | |
| Ratio | ... | 3.2 | 1.9 | 1.8 | 1.7 | 1.8 | 0.34 | 0.29 | 0.27 | |
| | -0.35 ppm | | | | | | | | | |
| As reported | 0 | 0 | 0 | 0 | .04 | 0 | 0.76 | 0.14 | 0 | |
| Corrected | 0 | 0 | 0.04 | 0.03 | 0.18 | 0 | 0.02 | 0 | 0 | |

^a LB = Long Beach, LADT = Los Angeles downtown, Bur = Burbank, Pas = Pasadena, Azu = Azusa, Pom = Pomona, SB = San Bernardino, Riv = Riverside, and Ana = Anaheim. Corrected data means LAAPCD data × 1.1 and ARB data × 0.8. Ratio = Corrected/As reported.

explain the fact that cities such as Pasadena, Azusa, and Pomona usually have higher oxidant levels than do locations which lie upwind of them, such as downtown Los Angeles.

Oxidant Levels. Table I shows that when LAAPCD data are appropriately corrected, the number of days on which the hourly oxidant concentration equals or exceeds 0.08 ppm is increased by at least 5% at the six Los Angeles County stations, and that the average increase is almost 20%. Table II shows that at these same six Los Angeles County stations, the number of hours ≥ 0.08 ppm is increased by at least 12% with the average increase being almost 30%. For Los Angeles County stations the increases observed relative to the first-stage episode criteria level of 0.20 ppm are substantially larger, though more variable. Thus, the number of days ≥ 0.20 ppm increases by 20–130% with the average increase being 50%, and the number of hours increases by 40–140% with the average increase being 60%.

Tables I and II also show that, if the data from the San Bernardino, Riverside, and Anaheim stations, which are referenced to the ARB 2% neutral buffered KI method, are appropriately corrected, then days ≥ 0.08 ppm decrease by an average of 20% and hours ≥ 0.08 ppm decrease by an average of 30%, whereas days and hours ≥ 0.20 ppm decrease by 23–70% and 46–80%, respectively.

Examination of the data in Tables I and II shows that, once the data have been appropriately corrected, the new second-stage episode criteria level of 0.35 ppm (formerly 0.40 ppm) has been exceeded more frequently at Pasadena, Azusa, and Pomona than it has at San Bernardino and Riverside, whereas the data as reported suggest that the converse is true. Also, the corrected data show that from 1971 through 1974, the new third-stage episode criteria level of 0.50 ppm (formerly 0.60 ppm) was exceeded only on eight days, once at Los Angeles downtown, once at Pasadena, on four days at Azusa, and twice at Upland. By use of data as reported, no third-stage levels were recorded at any of the LAAPCD stations, although the San Bernardino APCD reported two third-stage episodes at Upland.

Oxidant Dosages. Reliable assessment of the health effects of any pollutant should not be based simply on peak exposure levels, which are frequently brief in duration, but on cumulative dosage above some specified exposure level, where dosage is defined as the integral of the concentration of the pollutant over the time of exposure. This concept is illustrated in Figure 4, which presents the diurnal variation of oxidant levels (both as reported and corrected) at Upland on July 25, 1973. The shaded portion of the figure is the uncorrected Upland dosage above the old California 0.40 ppm second-stage episode level for oxidant. This area can be defined mathematically as follows:

$$\text{Dosage } (\geq \delta) = \int_{t_1}^{t_2} [f(t) - \delta] dt \quad (8)$$

where $f(t)$ is the dashed curve, which gives the diurnal variation of the uncorrected oxidant concentrations [$[Ox] = f(t)$], δ is the specified exposure level (0.40 ppm), and t_1 and t_2 (11:00 a.m. and 4:20 p.m.) are the times between which the oxidant concentration exceeded the exposure level δ .

Figure 5 contrasts the uncorrected and corrected Upland oxidant dosages for July 25, 1973, to those of Pasadena. Without correction, the Upland dosages substantially exceed those of Pasadena. With correction, the Pasadena dosages are almost as high as those in Upland.

The geographical extent of the elevated noontime oxidant dosages of July 25, 1973, can best be seen by constructing an oxidant contour map of that portion of the basin surrounded by a 1500-ft elevation barrier (33–35). Figures 6 and 7 present such maps, using data as reported and corrected data from 20 stations in the South Coast Air Basin. Comparison of the two

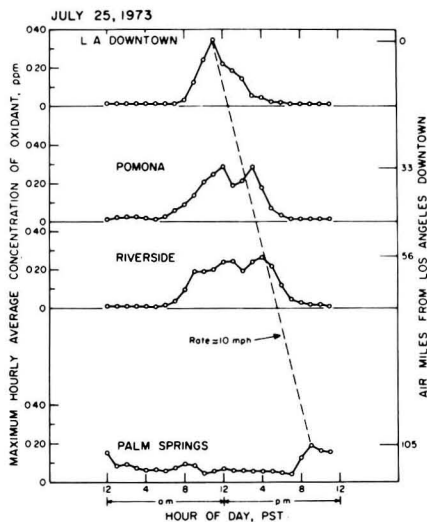


Figure 2. Diurnal variation July 25, 1973, of oxidant concentrations at air monitoring stations at Los Angeles downtown, Pomona, Riverside, and Palm Springs, Calif. Values are corrected data: Los Angeles downtown and Pomona $\times 1.1$ and Riverside and Palm Springs $\times 0.8$

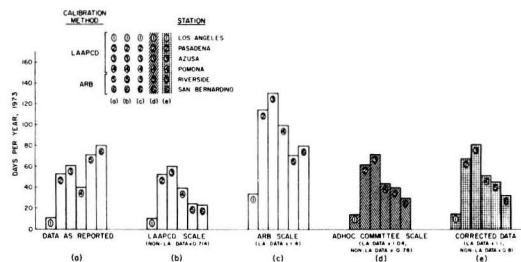


Figure 3. Number of days in 1973 on which hourly average oxidant concentration equaled or exceeded 0.20 ppm at six air monitoring stations in South Coast Air Basin (a) Data as reported; (b) LAAPCD scale—non-LAAPCD data (Riverside and San Bernardino) $\times 0.714$; (c) ARB scale—LAAPCD data (Los Angeles, Pasadena, Azusa, Pomona) $\times 1.4$; (d) Ad hoc committee scale—LAAPCD data $\times 1.04$, non-LAAPCD data $\times 0.78$; (e) corrected data—LAAPCD data $\times 1.1$, non-LAAPCD data $\times 0.8$

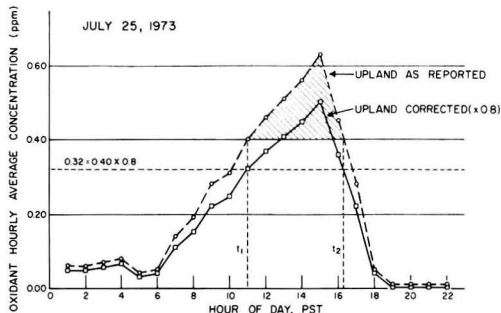


Figure 4. Diurnal variation of oxidant concentration (data as reported; corrected values—data $\times 0.8$) at Upland air monitoring station on July 25, 1973. Upland station is in San Bernardino Air Pollution Control District which used ARB oxidant measurement calibration method

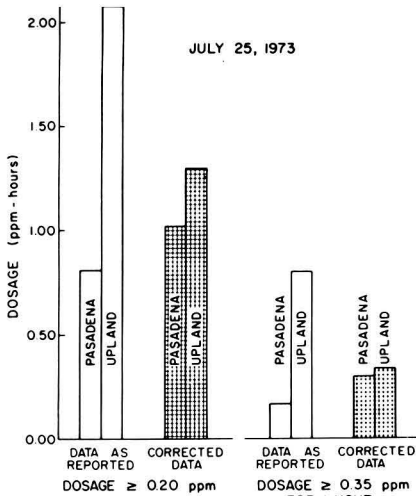


Figure 5. July 25, 1973, oxidant dosages greater than or equal to 0.20 and 0.35 ppm at Pasadena and Upland air monitoring stations (corrected data—Pasadena values $\times 1.1$ and Upland values $\times 0.8$)

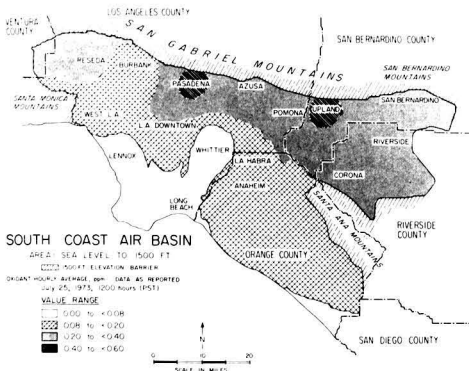


Figure 6. Uncorrected oxidant contour map, data as reported, of South Coast Air Basin between sea level and 1500 ft, 12 noon, July 25, 1973

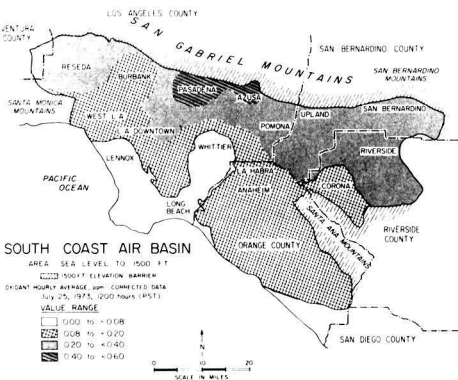


Figure 7. Corrected oxidant contour map (LAAPCD data $\times 1.1$, non-LAAPCD data $\times 0.8$) of South Coast Air Basin between sea level and 1500 ft, 12 noon, July 25, 1973

maps shows that the data as reported significantly overestimate the extent of the regions of high dosage, especially near the city of Upland. It also shows that at noon on July 25, 1973, the regions of high oxidant in the South Coast Air Basin lay just below the San Gabriel Mountains (Pasadena and Azusa) directly downwind from major population centers.

Figure 8 presents 1973 yearly oxidant dosages ≥ 0.20 ppm for six air monitoring stations in the South Coast Air Basin. As before, correction of the data produces significant shifts in relative dosages with the result that highest dosages occur at Pasadena and Azusa and not at Riverside and San Bernardino. Table III shows that this result is true for other levels, stations, and for 1974. Specifically, when the data are appropriately corrected, LAAPCD dosages ≥ 0.08 ppm increase by an average of 30%, and those ≥ 0.20 ppm increase by 40–200%. The decreases in the dosages experienced at non-LAAPCD stations are also pronounced. Dosages ≥ 0.08 ppm decrease on the average by 40%, whereas dosages ≥ 0.20 ppm decrease by 60–90%.

It is often assumed that, if a set of oxidant data and the air quality standards and health-warning episode levels based on those data both are scaled by the same factor, then the oxidant exposure above the scaled standard calculated using the scaled data will equal the oxidant exposure calculated using the old standard and the uncorrected data. For example, had the state's former second- and third-stage episode criteria levels, 0.40 and 0.60 ppm, respectively, been scaled down by a factor of exactly 0.8, to 0.32 and 0.48 ppm, respectively, then one might expect that the dosage above those corrected criteria levels, calculated using the scaled data, would equal the old dosage above the former standards, calculated using unscaled data.

This is not the case. For example, had the California second-stage episode criteria level (0.40 ppm) been lowered by a factor of exactly 0.8, then the new corrected dosages above the new corrected episode criteria level (0.32 ppm) would not have equaled the old uncorrected dosages. Instead, they would be lower than the old uncorrected dosages by 20%, that is, decreased by a factor of 0.8. This results from the fact that scaling both oxidant readings and standards by 0.8 is equivalent to multiplying Equation 8 by a constant, $k = 0.8$. Because this does not change the limits of integration (see Figure 4), the corrected dosage above the scaled standard equals the uncorrected dosage above the existing standard multiplied by the factor $k = 0.8$.

$$\begin{aligned} \text{Corrected Dosage } (\geq k\delta) &= \int_{t_1}^{t_2} [kf(t) - k\delta] dt \\ &= k \int_{t_1}^{t_2} [f(t) - \delta] dt = k \times \text{Uncorrected Dosage } (\geq \delta) \quad (9) \end{aligned}$$

Control Strategies. Uncorrected data show that the maximum hourly average oxidant level (0.63 ppm) recently measured in the South Coast Air Basin occurred at Upland on both July 25, 1973, and June 27, 1974. When corrected, this level becomes 0.50 ppm, a 20% reduction from the data as reported. Because this reduction is substantial, it is likely that in the South Coast Air Basin, attainment of the Federal Air Quality Standard for oxidant of 0.08 ppm for 1 h may be significantly less difficult than was first thought in 1973 when the EPA originally published its strategy (36) for the linear rollback of emissions of reactive hydrocarbons in the South Coast Air Basin. However, only a thorough reevaluation of South Coast Air Basin oxidant control programs (37) can determine whether the hydrocarbon control measures necessary to reduce the true peak hourly oxidant levels of ~0.5 ppm, not 0.6 ppm, to 0.08 ppm will be significantly less severe—technically and economically—than those previously proposed.

Socioeconomic Effects. Regulatory action taken by local APCD's, when oxidant levels reach the California episode criteria levels of 0.20, 0.35, and 0.50 ppm for 1 h, significantly affect the activities of private citizens, schools, organizations, businesses, and industries. For example, when oxidant levels reach 0.20 ppm (health advisory alert), APCD's advise that school children and health-sensitive individuals refrain from strenuous physical exercise; at 0.35 ppm (warning), traffic reductions and curtailment of industrial emissions are required; and at 0.50 ppm (emergency), businesses may be closed to reduce traffic, and industrial activities which release significant emissions, may be directed to cease operations (38).

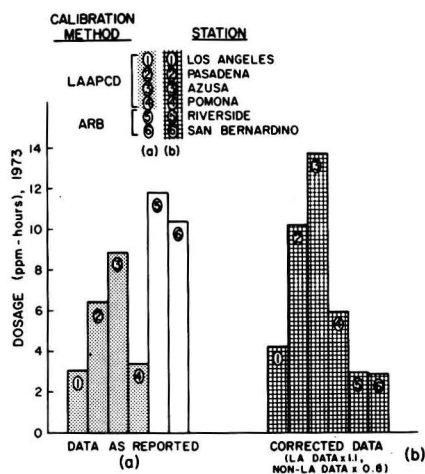


Figure 8. 1973 oxidant dosage greater than or equal to 0.20 ppm at six air monitoring stations in South Coast Air Basin; (a) data as reported; b) corrected data—LAAPCD data $\times 1.1$, non-LAAPCD data $\times 0.8$

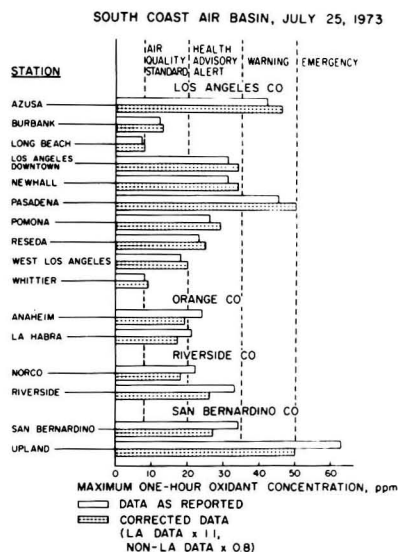


Figure 9. Maximum 1-h oxidant concentrations on July 25, 1973, at selected air monitoring stations in four South Coast Air Basin counties, showing data as reported and as corrected (LAAPCD data $\times 1.1$, non-LAAPCD data $\times 0.8$)

Figure 9 compares the maximum hourly average oxidant readings reported (39) on July 25, 1973, by 16 South Coast Air Basin air monitoring stations to the true readings which would have been reported had consistent ozone calibration methods been in use at that time. Figure 9 shows that the use of non-consistent oxidant data caused two Orange County air monitoring stations, Anaheim and La Habra, to report first-stage oxidant episodes which did not exist, whereas the West Los Angeles station in Los Angeles County failed to report a first-stage episode which did exist. Figure 9 also shows that, when a third-stage alert requiring emergency action was declared for Upland on July 25, 1973, one should also have been called for Pasadena, which also experienced an oxidant level of 0.50 ppm for 1 h.

Formation of a four-county Southern California Air Pollution Control District including Los Angeles, Orange, Riverside, and San Bernardino Counties on July 1, 1975 (40), as well as the continued possibility of a state legislatively mandated basinwide APCD (41), should ensure that oxidant episodes are reported throughout the region based upon measurements which are self-consistent.

Scientific Implications. Observations made in this paper are offered with the viewpoint that scientific investigators using the published data and interpreting the oxidant data across the South Coast Air Basin will wish to make appropriate changes in their data. For example, computer simulations of photochemical smog formation and transport in the Los Angeles basin should be reexamined. Specifically, models based partly on LAAPCD oxidant data and partly on non-LAAPCD data (42) have been validated against an inconsistent data base.

Finally, it is of considerable concern to both the scientific community and the public that air quality data and standards be credible. The credibility of air quality data and standards based on those data has already been strained by the NO_2 measurement controversy resulting from the Chattanooga Study (43). The present oxidant measurement controversy has not helped matters. It is essential that air pollution standards and control programs be based on consistent data obtained by valid experimental methods, mutually agreed upon by control agencies and research scientists.

Conclusions

The corrected South Coast Air Basin oxidant data clearly show that cities located below the southern slopes of the San Gabriel Mountains (Pasadena and Azusa) have significantly higher oxidant levels than cities located in the eastern portion of the basin (Riverside and San Bernardino) and that non-Los Angeles County oxidant dosages have been substantially lower than has been believed. These two conclusions significantly alter current views of the oxidant problem in the South Coast Air Basin and have important ramifications for the understanding and control of photochemical oxidant.

Acknowledgment

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Investigation of Solubilization of Plutonium and Americium in Soil by Natural Humic Compounds

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■ An investigation was conducted under simulated natural conditions to determine the solubilization of plutonium and americium in contaminated soil by humic compounds. The results indicate that the solubilization of plutonium and americium by fulvic acid—the more soluble humic compound—is slight. In no instance did the plutonium and americium concentrations in solution approach the drinking water limits. What little solubilization that occurs is probably due to complex formation and/or colloid peptization. The resulting solutions are unstable, and over a period of a few days, most of the plutonium and americium precipitate, either as a result of colloid coagulation or hydrolysis. Two other factors appear to limit the solubilization of these elements: only a relatively small fraction of the plutonium and americium seems to be readily soluble, and there is apparently a low saturation value for these elements in both water and fulvic acid solution.

The ability of humic compounds, i.e., humic and fulvic acids present in soils and natural waters, to enhance the solubilities of metal ions and hydrous oxides is well known. Ong et al. (1) have demonstrated that aluminum, iron, copper, zinc, and lead are solubilized by humic substances in water at concentrations of 4–40 ppm (expressed as carbon), the solubilities increasing with humic concentration and pH in the range 4–9. Shapiro (2) has observed that natural waters containing sufficient humic substances to be colored can contain 10^8 – 10^9 times as much iron as would be predicted from the solubility product; and smaller increases in solubilities of iron, copper, manganese, and nickel hydroxides have been reported by Rashid and Leonard (3) who also pointed out that these increases in solubility should enhance the migration of these metal ions. Despite some interpretations to the contrary (4), there is general agreement that solubilization is accomplished by the formation of complexes (1, 5, 6), and in their monograph, Schnitzer and Khan (5) have summarized the potentiometric, ion-exchange, conductometric, and polarographic evidence supporting this mechanism.

Humic substances are complex mixtures of high molecular weight organic species of unknown structure. They are generally classified on the basis of solubility: humic acid is the fraction that is soluble only in base, whereas the fraction soluble in both acid and base is known as fulvic acid. Humic acid and fulvic acid are similar structurally, differing mainly by virtue of the higher molecular weight and greater number of functional groups of the former (7). Of the two, fulvic acid is more effective in solubilizing iron and aluminum ions and hydrous oxides (8). Carboxyl and phenolic-OH groups are primarily responsible for complex formation (9), and it is likely that many of the complexes are chelates. Ong and Bisque (10) have pointed out that humic solutions may also be considered as sols of hydrophilic colloids, and as such, they are subject to coagulation by various electrolytes.

With the presence of plutonium and americium in soils as a result of fallout from weapons tests and releases from nuclear facilities, there is concern about their solubilization and transport in the natural environment. The ability of soil humic substances to solubilize other readily hydrolyzable but strong

complex-forming ions, such as iron, suggests that a similar phenomenon might occur with plutonium and americium. This paper reports the results of a laboratory study to determine the ability of humic solutions to solubilize these elements in contaminated soil under simulated natural conditions.

Experimental

The soil used in this study was obtained from a plutonium-contaminated area at the Rocky Flats Plant of the U.S. Energy Research and Development Administration. Although the chemical form of the plutonium and americium is not known, it is assumed to be the dioxide. This assumption is justified in view of the tendency of plutonium compounds to hydrolyze to the hydrous oxide and the presence of this plutonium in the soil for several years, thus allowing adequate time for hydrolysis to occur. The soil is an alluvial highly weathered sand and gravel whose fine (–200 mesh, $-74 \mu\text{m}$) fraction has a pH of 7.0–7.5 and consists of quartz (20–30%), orthoclase (20–30%), plagioclase (10–20%), calcite (0–15%), hornblende (0–4%), magnetite (trace), biotite (2–3%), chlorite (1–3%), secondary iron oxides (~1%), and montmorillonite clay (5–20%), with the smallest (–6.5 μm) fractions also containing feldspar (~30%) and layered silicates (20–30%). Because the soil contained many rocks, pebbles, and plant fragments, and because previous work had shown that the plutonium was concentrated in the smaller size fractions, only the $-74 \mu\text{m}$ size fraction was used in this study. Individual samples of this fraction used in this study had plutonium concentrations in the range 11–27 nCi/g and americium concentrations varying from 95 to 190 pCi/g.

The humic and fulvic acid fractions used in this study were kindly supplied by R. L. Wershaw of the U.S. Geological Survey, Denver, Colo., who extracted them from soil from a dry stream bed at the Rocky Flats plant site; thus, they should be representative of humic materials in this area. The extraction procedure, based on leaching the soil with 0.1 N NaOH, followed by acidification of the leach solution to precipitate humic acid and freeze-drying of the supernate to obtain fulvic acid, has been described in detail elsewhere (11). Elemental analyses of these humic and fulvic acid fractions are given in Table I. Their infrared spectra were similar to those published by Schnitzer (7).

Fulvic acid solutions (100 ppm) were made by dissolving the appropriate amount of fulvic acid in water and adjusting the pH to the desired value with dilute HCl or Na_2CO_3 solution after dissolution. (Early experiments indicated that dissolution of fulvic acid lowers the pH of the solution by one pH unit or more.) Humic acid was not soluble even to the extent of 10 ppm at any of the pH values of interest. Since it was felt that lower concentrations would not be effective, particularly in view of the reportedly lower ability of humic acid compared to fulvic acid in solubilizing metal ions, no soil extraction studies were conducted with humic acid.

Extractions consisted of shaking 1.0-g samples of contaminated soil with 40 ml of water or 100 ppm fulvic acid solution at the desired pH in 50-ml polycarbonate centrifuge tubes on a Burrell wrist-action shaker. The initial pH values were selected to encompass conditions to be expected in ground waters, and since the intent was to simulate natural conditions as closely as possible, there was no further pH adjustment

Table I. Analysis of Fulvic and Humic Acids

| | Fulvic acid, % | Humic acid, % |
|-----------|----------------|---------------|
| C | 36.50 | 36.04 |
| H | 5.76 | 4.02 |
| O | 43.70 | 31.40 |
| N (Dumas) | 2.93 | 2.97 |
| Dry ash | 10.18 | 24.51 |

after the extractions were begun. After each equilibration period, the tubes were centrifuged for 10 min at 10 000 rpm, and 5-ml samples of the supernate were withdrawn. These centrifuging conditions were calculated to separate particles somewhat smaller than 1 μm in size; hence, all suspended matter should be removed, but not necessarily all colloidal material. Aliquots of the supernate were evaporated on stainless steel planchets for analysis by alpha spectrometry using the 5.15 MeV alpha peak for plutonium and the 5.5 MeV peak for americium. Counting was on a Nuclear Data 4420 pulse height analysis system with ORTEC surface barrier detectors. This procedure gave a 95% confidence level of $\pm 6\%$ on the counting. During sampling, a pH determination was made on each solution using an Orion Model 801A digital "Ionalyzer" with a PolyMark No. 1808 combination pH electrode. Each centrifuge tube was then vigorously hand-shaken long enough to resuspend the precipitate and returned to the shaker for additional contacting.

On termination of the extraction experiments, the soil residues were separated by centrifugation and analyzed for plutonium and americium, and the supernates were analyzed spectrophotometrically for fulvic acid concentration. The soil analysis consisted of leaching with 1:1 $\text{HNO}_3\text{-HCl}$ solution containing a small amount of HF and separating plutonium from americium by anion exchange. The americium solution was mounted directly and counted using the pulse height analysis equipment described above; the plutonium solution was extracted with a solution of 0.5 M thenoyltrifluoroacetone (TTA) in xylene, which was then mounted and counted as above. (There was no addition of liquid to replenish the amount removed in sampling; hence, the volume decreased 5 ml with each successive sampling.) Each experiment was run in triplicate at ambient temperature ($\sim 25^\circ\text{C}$).

The concentrations of the fulvic acid solutions were determined spectrophotometrically with a Beckman DK-2A spectrophotometer at 350 nm, and a Perkin-Elmer Model 567 spectrophotometer was used to obtain the infrared spectra.

A series of preliminary experiments established that adsorption of plutonium and americium onto the walls of the centrifuge tubes was insignificant in the pH range of these studies. Another series of runs indicated that maximum plutonium uptake occurred after 5–24 h of extraction, and this information was used in setting the sampling periods for the principal experiments.

The first series of runs consisted of extractions with water and fulvic acid solutions at initial pH values of 5, 7, 8, and 9 for 357 h, with analysis of the supernate at appropriate intermediate time periods. At the conclusion of these runs, the remaining supernate was decanted, and 40 ml of fresh water or fulvic acid solution of the original pH was added to the soil residue and the contacting was repeated, again with sampling at intermediate time periods. This reextraction procedure was repeated twice more, each time with 40 ml of the corresponding fresh solution. At the conclusion of the third reextraction run, the entire soil residue was analyzed for plutonium and americium.

Another series of runs involving more extensive multiple extraction further defined the behavior of plutonium and americium in the system. One-gram samples of contaminated

soil were contacted with 40 ml of water or 100 ppm fulvic acid at pH 9, the pH at which solubilization was maximum in the previous series. After a 24-h extraction, the tubes were centrifuged and sampled as before. The remaining supernate was decanted and replaced with 40 ml of the corresponding fresh solution, and extraction resumed. This procedure was repeated a total of seven times. In addition, the supernates from the first extraction, after sampling, were contacted for two successive 24-h periods, each time with fresh 1-g samples of contaminated soil.

The data from all these experiments are reported in terms of the extraction coefficient, defined as the plutonium (americium) concentration in the supernate (in pCi/ml) divided by the concentration in the soil (in pCi/g). Although, as stated previously, the activity in the soil samples was variable, the analyzed value for each individual soil sample was used in the calculations.

Results and Discussion

The most obvious finding from these experiments is the very low solubilization of plutonium and americium under all conditions studied. Even after repeated extraction of contaminated soil for periods as long as 357 h with solutions at various pH values and containing higher fulvic acid concentrations than normally found in ground waters, the plutonium solubility was generally between 20 and 200 pCi/l. The maximum plutonium concentration, 390 pCi/l., obtained in the third reextraction at pH 9, is only 23% of the maximum permissible concentration of plutonium-239 in drinking water (12). Concentrations of americium in the supernates were generally in the 5–30 pCi/l. range, with the maximum value of 81 pCi/l. being 6% of the maximum permissible concentration of americium in drinking water (12). Moreover, since these maximum values decreased with further extraction, they do not represent the amounts of these elements permanently solubilized.

The data from the primary extraction studies at pH 5 and 9 are reported in Table II in terms of the extraction coefficient.

The extraction data at pH 7 and 8 are similar in magnitude to those at pH 5 and 9, but are not included since they do not indicate any statistically significant enhancement of solubilization in fulvic acid under any of the conditions studied. (All decisions regarding statistically significant differences were made by use of Student's T test at the 95% confidence level.) It will be noted in Table II that maximum solubilization of plutonium and americium usually occurs after 5–24 h of the initial extraction, after which the concentration of both elements decreases significantly. This behavior suggests that the dissolved species were adsorbed on the container walls, but early experiments in which the containers were exhaustively treated with hot concentrated nitric acid to remove adsorbed material indicated that such adsorption was insignificant. However, in other experiments in which solutions that had been contacted with contaminated soil for a period and then decanted into fresh containers and agitated for an additional period in the absence of soil, the plutonium and americium (and possibly other cations, such as iron and aluminum) that had been solubilized from the soil eventually formed a gelatinous precipitate.

This observation suggests that these elements were actually dispersed in a colloidal form that coagulated with time. (The centrifugation procedure would not remove particles in the colloidal size range, i.e., smaller than about 1 μm .) Also, the plutonium and americium could be adsorbed on colloidal clay particles in the solution, which coagulated and precipitated. Another possible explanation is that these elements initially were actually in solution, possibly as fulvate complexes, but the complexes were unstable, resulting in slow hydrolysis and precipitation. The data do not permit a choice between these

alternatives, but from a phenomenological standpoint, it is clear that the plutonium and americium are not permanently solubilized from the soil under these conditions.

The americium extraction coefficients are generally higher than the values for plutonium by one to two orders of magnitude. Americium dioxide is more soluble than its plutonium analogue; moreover, the trivalent americium ion—the only oxidation state occurring in solution under normal conditions—is less prone to hydrolysis than the tetravalent plutonium ion. Apparently these effects predominate over the greater complex-forming ability of the plutonium ion. Hence it would appear that complexing by fulvic acid is not the major factor in solubilization, a conclusion that is supported by the observed minor enhancement in plutonium and americium solubilities in fulvic acid solutions compared to water, and also by the observation that there was not a direct correlation between plutonium and americium concentrations and fulvic acid concentrations in the supernates.

After peaking in the 5–24-h period, the decrease in concentration with further extraction is not as great for americium as for plutonium, suggesting that hydrolysis may be involved in the decrease. Since americium and plutonium par-

allel one another in behavior, it seems likely that both are solubilized and subsequently precipitated by the same mechanism.

Since this experiment is a simulation of natural conditions, no attempt was made to control pH after the initial adjustment. Therefore, the pH of the solutions changes because of soil buffering and, as can be seen in Table II, soon assumes a value between 6.5 and 7.5 regardless of the initial pH. This final pH value without doubt has a greater influence on the behavior of plutonium and americium than does the initial pH, hence the relative constancy of extraction coefficients at various initial pH values except at pH9.

The results of this study indicate that fulvic acid does not increase the solubilization of plutonium and americium to a significant extent under the conditions studied. Only in the pH 9 runs are there consistent statistically significant differences (as determined by Student's T test) between water and fulvic acid, and a slight enhancement indeed occurs. The higher plutonium and americium extraction coefficients at pH 9 are probably due at least in part to the presence of fulvic acid, but the possible contribution of carbonate ions, added as Na₂CO₃ to adjust the initial pH, must also be taken into

Table II. Soil Extraction Results^a

| Time, h | Water | | | Fulvic acid | | | |
|---------------------|---|--------------|--------------|---|--------------------------|------------|-----|
| | Extraction coeff × 10 ⁶ ^b | | | Extraction coeff × 10 ⁶ ^b | | | |
| | Pu | Am | pH | Pu | Am | pH | |
| | | | Initial pH 5 | | | | |
| Initial extraction | 5 | 7.4 (±1.3) | 160 (±40) | 7.3 | 14 (±0.57) ^d | 220 (±85) | 7.5 |
| | 24 | 8.8 (±0.70) | 120 (±42) | 7.1 | 10 (±2.9) | 160 (±76) | 7.4 |
| | 95 | 6.1 (±2.4) | 110 (±96) | 6.9 | 3.4 (±0.30) | 74 (±38) | 6.9 |
| | 190 | 2.0 (±0.81) | 63 (±23) | 6.8 | 2.7 (±0.61) | 72 (±12) | 6.9 |
| First reextraction | 357 | 1.1 (±0.37) | 47 (±3.1) | 6.9 | 2.7 (±0.57) | 84 (±7.0) | 7.0 |
| | 5 | 2.7 (±0.26) | 82 (±24) | 7.8 | 4.2 (±0.91) | 100 (±29) | 7.8 |
| | 23 | 2.5 (±0.25) | 54 (±22) | 7.4 | 4.5 (±0.81) | 110 (±47) | 7.4 |
| | 94 | 1.4 (±0.15) | 42 (±7.2) | 7.0 | 1.5 (±0.10) | 39 (±7.8) | 6.6 |
| Second reextraction | 190 | 2.0 (±0.70) | 100 (±7.2) | 7.0 | 2.0 (±0.21) | 57 (±20) | 6.9 |
| | 5 | 0.98 (±0.32) | 38 (±2.1) | 6.8 | 3.2 (±0.36) ^d | 110 (±54) | 7.3 |
| | 24 | 2.2 (±1.6) | 58 (±14) | 7.1 | 6.1 (±2.2) | 69 (±18) | 7.2 |
| | 95 | 1.2 (±0.39) | 48 (±17) | 7.1 | 1.4 (±0.25) | 50 (±18) | 6.8 |
| Third reextraction | 167 | 1.5 (±0.52) | 94 (±58) | 7.0 | 2.5 (±0.45) | 110 (±10) | 6.9 |
| | 5 | 1.2 (±0.37) | 120 (±43) | 6.7 | 4.1 (±1.1) ^d | 120 (±47) | 7.0 |
| | 26 | 0.87 (±0.29) | 45 (±10) | 6.9 | 3.6 (±1.3) | 120 (±55) | 6.8 |
| | 95 | 0.39 (±0.10) | 36 (±3.5) | 7.0 | 2.3 (±1.5) | 92 (±26) | 6.9 |
| 166 | 1.1 (±0.59) | 91 (±57) | 7.0 | 1.0 (±0.18) | 56 (±37) | 6.8 | |
| | | | Initial pH 9 | | | | |
| Initial extraction | 5 | 9.3 (±0.12) | 170 (±35) | 7.7 | 11 (±1.1) | 280 (±23) | 7.8 |
| | 24 | 9.0 (±2.6) | 130 (±32) | 7.5 | 8.7 (±1.1) | 170 (±25) | 7.4 |
| | 95 | 2.5 (±0.35) | 97 (±35) | 7.2 | 4.6 (±0.95) | 82 (±51) | 7.0 |
| | 190 | 1.9 (±0.50) | 79 (±53) | 7.1 | 3.2 (±0.61) | 100 (±53) | 7.0 |
| | 357 | 1.6 (±0.26) | 68 (±16) | 7.1 | 1.6 (±0.31) | 52 (±25) | 7.1 |
| First reextraction | 5 | 2.3 (±0.26) | 80 (±23) | 7.9 | 6.5 (±0.22) ^d | 150 (±17) | 8.0 |
| | 23 | 3.1 (±0.89) | 97 (±31) | 7.6 | 4.9 (±0.72) | 170 (±66) | 7.5 |
| | 94 | 1.2 (±0.12) | 55 (±25) | 7.0 | 2.4 (±0.42) ^d | 84 (±57) | 7.1 |
| | 190 | 1.0 (±0.06) | 110 (±48) | 7.2 | 2.3 (±0.15) ^d | 35 (±9.5) | 7.0 |
| Second reextraction | 5 | 2.4 (±0.75) | 71 (±23) | 7.5 | 3.6 (±0.60) | 180 (±60) | 8.1 |
| | 24 | 2.7 (±1.7) | 67 (±32) | 7.7 | 11 (±0.69) ^d | 200 (±69) | 8.2 |
| | 95 | 2.3 (±0.25) | 54 (±12) | 7.6 | 12 (±2.1) ^d | 190 (±73) | 8.0 |
| | 167 | 1.9 (±0.32) | 84 (±20) | 7.5 | 8.7 (±1.8) ^d | 120 (±33) | 8.0 |
| Third reextraction | 5 | 6.3 (±0.74) | 150 (±15) | 7.5 | 18 (±1.7) ^d | 460 (±100) | 8.1 |
| | 26 | 4.1 (±1.3) | 130 (±32) | 7.7 | 17 (±4.0) ^d | 320 (±150) | 7.5 |
| | 95 | 2.3 (±0.76) | 110 (±10) | 7.6 | 4.7 (±0.81) ^d | 110 (±10) | 7.4 |
| | 166 | 2.1 (±0.35) | 72 (±19) | 7.5 | 3.4 (±0.46) ^d | 72 (±10) | 7.3 |

^a One-gram samples of contaminated soil extracted with 40-ml solution at approximately 25 °C. ^b The extraction coefficient is defined as pCi Pu(Am)/ml solution divided by pCi Pu(Am)/g soil. All values are means of triplicate runs unless noted otherwise. Numbers in parentheses are standard deviations. ^c Mean of duplicate runs. ^d Denotes values statistically higher than the corresponding values in water.

account. Carbonate ions are known to complex plutonium (13), and the fulvic acid solutions, because of the buffering effect, required more Na_2CO_3 for pH adjustment than water. Hence the enhanced solubilization may be due to the presence of both carbonate and fulvate ions. It is doubtful, however, that carbonate is a significant factor in solubilizing plutonium from the soil; Bondiotti et al. (14) have obtained evidence indicating that carbonate complexing is not sufficient to stabilize plutonium (IV) as a soluble monomer. The enhancement is not surprising since both fulvate and carbonate are anions of very weak acids and would not be present in appreciable concentrations at lower pH values. Because the pH values of the water solutions are similar to those of the fulvic acid solutions at all stages of extraction, pH appears to be a secondary influence, only affecting the dissociation of the acids present.

The effect of fulvic acid may be greater than these results suggest, since the soil samples themselves contained fulvic acid, some of which dissolved during extraction and hence could influence solubilities even in the water extractions. This possibility was confirmed by analysis of solutions after extraction; a few of the water samples contained as much as 125 ppm fulvic acid. In any case, however, the ability of fulvate and/or carbonate ions to solubilize these elements is very slight and probably proceeds by formation of a weak complex, which is then dissolved or peptized into solution. If dissolved, it is slowly hydrolyzed and precipitated; if peptized, it is eventually removed from solution by coagulation. It is possible, of course, that both mechanisms are operative.

Questions are raised by the data in Table II, one of the more important being whether plutonium and americium solubilities are limited by the amount of these elements available for solubilization or whether the limit is imposed by saturation of the solution. From a practical standpoint, the question of whether successive 24-h extractions of a given soil sample with fresh solution would continue to remove these elements at the

initial rate is of interest; if so, this could have a significant effect on the concentration of plutonium and americium in ground waters. Additional studies were made to answer this question, and the results are given in Tables III and IV.

The data in Table III indicate that successive 24-h extractions of the same soil sample with fresh solution increase the total amount of plutonium and americium solubilized, compared to that resulting from extended contact with the same solution. The concentrations generally decrease with succeeding extractions, however, suggesting that only part of the plutonium and americium is in an available form. After the eight contacts shown in Table III, a cumulative total of 0.24% of the plutonium and 0.63% of the americium was solubilized. The concentration in succeeding solutions would be expected to decrease even further, and it is probable that at some point the amount of plutonium and americium solubilized would be negligible.

There is also evidence that the solutions become saturated with plutonium and americium, as shown in Table IV. Successive 24-h extractions using the same solution and fresh samples of contaminated soil do not result in an increase in the amount of these elements solubilized. There is no statistically significant difference (as determined by Student's T test) in the plutonium and americium concentrations achieved in any of the three extractions, suggesting that there is a limit on the amount of these elements that can be held in solution, and that this limit is quite low. This observation is significant in terms of the natural environment, since it indicates that ground water, as it moves through the soil both horizontally and vertically, will not achieve high concentrations of plutonium and americium by continued contact with fresh soil. There is an increase in fulvic acid concentration; however, after the third extraction the fulvic acid concentrations of all the solutions were 500–700 ppm. The data in Table IV further indicate the negligible influence of fulvic acid on plutonium and americium solubilization.

Table III. Successive 24-h Extractions with Fresh Solutions at pH 9^a

| Extractions | Water | | | Fulvic acid | | |
|-------------|-----------------------------------|-------------------|-----|-----------------------------------|------------------|-----|
| | Extraction coeff $\times 10^{6b}$ | | | Extraction coeff $\times 10^{6b}$ | | |
| | Pu | Am | pH | Pu | Am | pH |
| First | 13 (± 1.6) | 240 (± 25) | 8.5 | 18 (± 3.7) | 390 (± 83) | 7.5 |
| Second | 9.0 (± 2.8) | 170 (± 86) | 8.2 | 9.9 (± 3.7) | 230 (± 47) | 7.9 |
| Third | 7.7 (± 1.5) | 140 (± 31) | 8.6 | 8.1 (± 2.7) | 200 (± 20) | 7.6 |
| Fourth | 11 (± 5.0) | 230 (± 91) | ... | 6.3 (± 0.87) | 160 (± 40) | ... |
| Fifth | 7.2 (± 1.3) | 250 (± 160) | ... | 5.0 (± 2.1) | 170 (± 22) | ... |
| Sixth | 5.4 (± 4.0) | 96 (± 50) | 8.7 | 5.9 (± 2.5) | 150 (± 13) | 7.4 |
| Seventh | 3.6 (± 0.59) | 83 (± 8) | 8.9 | 4.4 (± 0.86) | 140 (± 24) | 7.4 |
| Eighth | 4.2 (± 0.95) | 110 (± 32) | 8.8 | 4.2 (± 2.2) | 130 (± 42) | 7.6 |

^aThe same 1-g aliquot of soil was contacted every 24 h with 40 ml of fresh solution at pH 9 and approximately 25 °C. ^bThe extraction coefficient is defined as pCi Pu(Am)/ml solution divided by pCi Pu(Am)/g soil. All values are means of triplicate runs. Numbers in parentheses are standard deviations.

Table IV. Successive 24-h Extractions with Fresh Soil^a

| Extractions | Water | | | Fulvic acid | | |
|-------------|-----------------------------------|-------------------|-----|-----------------------------------|-------------------|-----|
| | Extraction coeff $\times 10^{6b}$ | | | Extraction coeff $\times 10^{6b}$ | | |
| | Pu | Am | pH | Pu | Am | pH |
| First | 13 (± 1.6) | 240 (± 25) | 8.5 | 18 (± 3.7) | 390 (± 83) | 7.5 |
| Second | 17 (± 1.8) | 340 (± 110) | 7.7 | 20 (± 2.0) | 330 (± 140) | 7.8 |
| Third | 12 (± 3.5) | 250 (± 120) | 8.6 | 17 (± 7.5) | 300 (± 96) | 7.6 |

^aOriginal solutions were at pH 9. After contacting 40 ml of solution with a 1-g aliquot of soil for 24 h, 5 ml of supernate were sampled for analysis. The remaining 35 ml of supernate were transferred to fresh soil for the second extraction. A similar procedure was followed for the third extraction. ^bThe extraction coefficient is defined as the pCi Pu(Am)/ml solution divided by the pCi Pu(Am)/g soil. All values are means of triplicate runs. Numbers in parentheses are standard deviations.

It should not be inferred from these conclusions that plutonium and americium do not react with fulvic acid. Bondiotti and coworkers (14) have found that plutonium does indeed react with natural fulvates to form insoluble complexes. Thus fulvic acid tends to remove plutonium from solution rather than enhance its solubility—a finding consistent with the results of the present study.

Extrapolation of these laboratory results to the natural environment can be perilous. There can be long-term effects not detected in short-term experiments, such as weathering and the action of microbacteria and plant life. Nevertheless, it is felt that this investigation has isolated and defined the behavior of fulvic acid toward plutonium and americium in soils of this specific type at this location. The applicability of these data to other types of soil has not been established. Keeping these limitations in mind, it seems reasonable to conclude that to the degree they are applicable to the natural system, these results indicate that soil humic compounds are not a major factor in the solubilization of plutonium and americium in Rocky Flats soil.

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Efficient Collection of Polycyclic Organic Compounds from Combustion Effluents

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■ A method for the collection of combustion effluents by use of a solid polymeric adsorbent is described. The adsorbent sampler described is considerably more efficient than the commonly used impinger methods and gives a quantitative collection of polycyclic organic compounds, together with quantitative recovery of the trapped species by an efficient solvent extraction technique. This sampling system may be used to collect combustion effluents at any temperature; a heat exchanger is incorporated to ensure that sampled hot gases are collected at an appropriately reduced temperature. It appears that the sampling system is unaffected by sulfur oxides, which can cause serious problems for conventional impinger collection methods. The validation studies described include laboratory simulations of combustion emissions and emission sampling from a multi-fuel 50-hp Scotch-Marine fire-tube boiler, together with limited field trials.

Polycyclic organic materials (POM) are emitted in trace quantities by a wide variety of natural and man-made sources (1). Because some POM compounds are carcinogenic (1-4), there is widespread interest in determining the quantity of these compounds emitted by various sources and the influence of various system parameters on these emissions. One problem encountered in determining emissions of polycyclic organic compounds is selection of a reliable sampling train for collection of these compounds.

Previous studies of POM have generally been limited to collecting the compounds by the EPA Method 5 procedure

(5). Unfortunately, Method 5 was primarily designed to collect and determine particulate mass emissions from combustion sources without regard to the chemical nature of species collected. Doubts have frequently been expressed regarding the collection of volatile and reactive organic compounds by this procedure; yet, no other method has previously been demonstrated to be more effective for the collection of these species.

The present work describes a new technique for the collection of organic combustion effluents, which is particularly effective for the quantitative collection of POM. This method depends upon adsorption of these organic species by a column of chromatographic adsorbent. Similar techniques have been used for collection of ambient pollutants with good results (6-8).

Sampling Equipment and Procedure

Three sampling trains were used in this investigation of POM sampling techniques: standard EPA Method 5 sampling train, a high-volume version of the Method 5 sampling train, and the adsorbent sampling system. The latter two sampling trains were developed by Battelle as a means to eliminate problems encountered when doing POM sampling with the Method 5 sampling train.

Method 5 Sampling Systems. The standard EPA Method 5 rig was that specified in the *Federal Register* of August 17, 1971. The only deviation from EPA-specified procedures was in sample recovery—a methylene chloride wash of the probe and impingers was added (EPA specified only an acetone wash of the probe and a water and acetone wash of the impingers).

The high-volume Method 5 sampling system was developed by Battelle to provide for obtaining a larger sample without increasing the sampling time (9). The components for the high-volume rig were similar in shape and function to the components of the standard Method 5 rig but were enlarged to provide for a 5–6-cfm flow rate (compared to 0.75 cfm of the standard Method 5 rig).

Adsorbent Sampling System. The adsorbent sampler which was developed in this program is shown schematically in Figure 1. The stack gases are sampled isokinetically by a sampling probe and passed through a heated filter, as described in EPA Method 5. Immediately after leaving the hot filter, the emissions pass into the cooling coil (120 × 0.8 cm) of the adsorbent sampler and then pass through a Pyrex frit and into a cylindrical column of Tenax adsorbent (7 × 3 cm containing 12 g of Tenax). The flow rate through the adsorbent sampler is typically 14 l. min⁻¹. The cooling coil and Tenax adsorbent are maintained at a constant temperature by means of a thermostated circulating water bath.

The incoming gases are cooled to maintain adsorbent efficiency; yet, the adsorbent is maintained above ambient temperature to preclude condensation of the large quantities of water vapor present in all combustion effluents. The gases leaving the sampler are drawn through an aqueous impinger, a Drierite trap, and dry gas meter by a Gast-0522 vacuum pump (as in Method 5 sampling). Thus, essentially, the new adsorbent sampling system consists of the standard EPA train with the adsorbent sampler located between the filter and the impingers. With this system, filterable particulate can be determined from the filter catch and the probe wash according to Method 5, whereas the POM can be determined from the analysis of the filterable particulate and the adsorbent sampler catch. The impingers are only used to cool and dry the stack gases before they enter the dry-gas meter, and their contents are discarded.

At the conclusion of the sampling run, the adsorbent sampler is sealed with a 15-mm Solv-Seal cap and a 28/12 ball-joint stopper and stored in darkness prior to solvent extraction of the organic materials.

Sample Recovery and Analysis

Sample extraction from the adsorbent sampler is achieved by means of continuous extraction with pentane (see later) with a demountable extraction apparatus which is shown schematically in Figure 2. Pentane, 100 ml, is required to achieve extraction of an adsorbent sampler. Sample recovery from the Method 5 impinger solutions was made by methylene chloride extraction, to which an acetone and methylene chloride impinger rinse was added. The sampling probes and hot filters from all three sampling systems were subjected to methylene chloride extraction. Internal standards are added to the combined extracts from each sampling train prior to volume reduction to approximately 1 ml by rotary evaporation and Kuderna-Danish evaporation. The extract is subjected to a Rosentype liquid chromatography separation (10) to isolate the POM fraction before carrying out gas chromatographic-mass spectrometric (GC-MS) analysis. Gas chromatographic separation is achieved using a 14 ft × 2 mm, 2½% Dexil 300 column programmed from 170 to 350 °C at 4 °C min⁻¹.

Separation of the benzpyrene isomers is routinely accomplished using a 1-ft 1% *N,N'*-bis(*p*-methoxybenzylidene)- α,α' -bi-*p*-toluidine column isothermal at 130 °C (11). Mass spectrometric analysis is carried out with a Finigan 3200 quadrupole mass spectrometer with a chemical ionization source; methane is routinely used as the carrier and reagent gas. Data acquisition is accomplished with a

System Industries 150 data acquisition system, and quantification of the POM compounds present is accomplished with a Digital PDP8 computer.

This mass spectrometric-computer quantification procedure makes use of specific absolute ion currents (12). The basis for the quantification procedure is to initially obtain the computer reconstructed gas chromatogram and mass spectrum in the normal fashion; this reconstructed gas chromatogram is then displayed on the CRT terminal, and an overlay for the protonated molecular ion of the POM of interest is superimposed. This overlay represents the ion current corresponding to that specific POM molecular weight plus 1 mass unit. If there is an area in the reconstructed gas chromatogram where the overlay indicates that this mass number is prevalent, the mass spectrum of

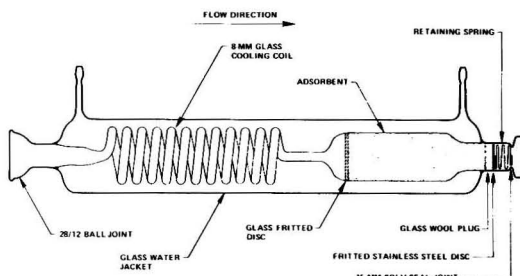


Figure 1. Adsorbent sampling system

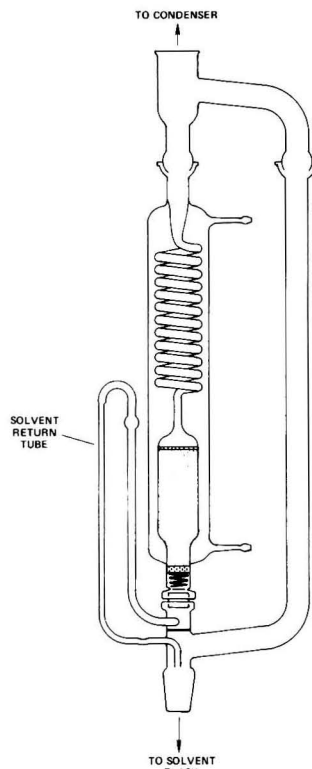


Figure 2. Continuous extraction assembly for adsorbent sampler

this peak is displayed on the CRT unit, and the presence of the POM may be confirmed. If the POM is found to be present at a correct relative retention time to the internal standards, the computer then sums the ion current due to all important ions in the POM's mass spectrum which represents the area of the peak of interest. Quantification of each POM is achieved by ratioing its ion current to that of an internal standard of known concentration. The relative ionization efficiencies of the internal standards and many POM species were previously determined, and the appropriate factor is used in quantification.

This quantification technique overcomes the problems associated with interfering or overlapping peaks and poor baseline separations since these interfering species would usually have different molecular weights. Isomeric compounds such as pyrene and fluoranthrene which have the same molecular weight can be quantified easily since they are very adequately separated by gas chromatography and their order of elution is known.

To obtain optimum sensitivity during the gas chromatographic-mass spectrometric analyses, the ionization voltage must be adjusted at various stages during the analysis. This adjustment necessitates the incorporation of three internal standards so that an internal standard would elute between each ionization adjustment. The internal standards chosen were 9-methylanthracene, 9-phenylanthracene, and 9,10-diphenylanthracene. It was fortuitous that 9,10-diphenylanthracene elutes almost coincident with the benz(a)pyrene/benz(e)pyrene isomers, giving a very accurate marker when searching for these important compounds. The relative retention times of other POM species to one or more of the internal standards are generally sufficiently well known to permit specific compound identification when the mass spectra are displayed.

This ion integration technique has proved to be far superior to GC for the analysis and quantification of POM because of its very high selectivity; it also offers a very significant advantage in speed of data handling.

Results of Laboratory and Field Trials

The validation of the adsorbent sampler for collection of polycyclic aromatic compounds was carried out by means of laboratory studies followed by sampling experiments using a 50-hp oil/gas fired Scotch-Marine fire-tube boiler, in addition to limited field trials.

Laboratory Validation Studies. Laboratory validation studies involved setting up an adsorbent sampler to collect air drawn through a 500 °F tube furnace. A precisely measured quantity of polynuclear compounds in a few microliters of methylene chloride solution was then injected into the inlet of the adsorbent sampler, and heated air was passed through the system for at least an hour. Following solvent extraction of the sampler, a suitable internal standard was added, and analysis for the spiked polynuclear compound was made by GC-MS analysis.

Preliminary experiments were carried out to determine the most suitable solvent for extraction of the adsorbent sampler. Extraction was attempted with methylene chloride, acetone, methyl alcohol, *p*-dioxane, pentane, cyclohexane, benzene, and toluene; only saturated hydrocarbons proved entirely suitable because of partial Tenax solubility in more polar solvents. Pentane was the most suitable solvent; its high volatility minimized sample loss during extraction. The relatively low extraction efficiency of pentane is overcome by means of continuous solvent extraction over 24 h, as shown in Figure 2.

Initial validation experiments involved sampling and recovery of measured quantities of anthracene; during this work the temperature of the sampler was allowed to rise to

approximately 200 °F, but quantitative anthracene recovery was always obtained.

Subsequent validation experiments were carried out with the sampler at 130 °F with pyrene, chrysene, perylene, benz(ghi)perylene, and coronene; these compounds are representative of commonly encountered POM species. Ten thousand nanograms of each of these compounds were separately sampled over a 2-h time period; following pentane extraction and addition of internal standard, the POM compound was quantified by GC-MS using specific absolute ion current integration. The results of several representative laboratory validation experiments are given in Table I.

Validation Studies with Emissions Generated by a 50-hp Scotch-Marine Fire-Tube Boiler. Emissions generated by a 50-hp Scotch-Marine fire-tube boiler were collected by different parallel combinations of the adsorbent sampling system and the two Method 5 sampling trains. The boiler stack had two sampling ports so that simultaneous sampling could be carried out for comparative evaluations of the adsorbent sampler and the impinger trains. The fuels used were either 1% sulfur residual oil or natural gas, and the boiler was normally fired at 80% load and 20% excess air.

Analysis for POM species was carried out as described earlier. Up to six abundant compounds were usually present, including anthracene, pyrene, fluoranthene, chrysene, benz(a)anthracene, benzfluoranthenes, and benzpyrenes; 10 or more less abundant species were often present in addition. To simplify the comparative evaluations of the three sampling trains, the total quantity of all detectable POM species was determined in each case and is expressed in $\mu\text{g}/\text{m}^3$.

Preliminary Validation Experiments—Residual Oil. Preliminary validation experiments in the boiler included comparative evaluations of the three sampling systems described earlier. The standard Method 5 sampling train was operated for 3 h, while each of the other trains was operated for 1 h during the same sampling period. GC-MS analysis showed that the total POM loading for each of the three systems was as follows: EPA Method 5, $-4.2 \mu\text{g}/\text{m}^3$; high-volume Method 5, $-5.6 \mu\text{g}/\text{m}^3$; and adsorbent sampler, $-55.2 \mu\text{g}/\text{m}^3$.

These results indicate a relatively good agreement between the two impinger methods, but demonstrate the apparent higher collection efficiency of the adsorbent sampler sampling train.

In a subsequent validation study, the above experiment was repeated under similar boiler operating conditions, with the exception that an additional adsorbent sampler was located downstream of the third impinger of the EPA Method 5 sampling train. The total load of POM in each sampling train as determined by GC-MS is as follows: adsorbent sampler, $-12.2 \mu\text{g}/\text{m}^3$; EPA Method 5, $-0.15 \mu\text{g}/\text{m}^3$; adsorbent sampler backup to EPA Method 5, $-1.4 \mu\text{g}/\text{m}^3$; and high-volume Method 5, $-0.19 \mu\text{g}/\text{m}^3$.

Table I. Recovery of POM from Adsorbent Sampler

| POM | Spiked, ng | Sample #1 av % recovery | Sample #2 av % recovery | Sample #3 av % recovery |
|-------------------|------------|-------------------------|-------------------------|-------------------------|
| Pyrene | 10 000 | 91 ± 3 | 98 ± 4 | 104 ± 4 |
| Chrysene | 10 000 | 90 ± 5 | 92 ± 5 | 106 ± 5 |
| Perylene | 10 000 | 91 ± 4 | 105 ± 5 | 102 ± 6 |
| Benz(ghi)perylene | 10 000 | 101 ± 10 | 106 ± 10 | 103 ± 7 |
| Coronene | 10 000 | 80 ± 7 | 92 ± 8 | 100 ± 14 |

Again, there is reasonable agreement between the impinger methods, and the adsorbent sampler appears to be considerably more efficient than either. The adsorbent sampler backup to Method 5 collected appreciably more than the impinger train itself; it is surprising that the total POM collected with the EPA Method 5 plus the adsorbent sampler backup did not more nearly equal the POM loading of the parallel adsorbent sampler. It would appear that this may be due to losses in the impinger train itself, possibly as a result of interaction of POM with sulfur oxides in the impingers. To minimize possible interferences from sulfur oxides, two sampling experiments were subsequently conducted using very low sulfur fuels.

Validation Experiments—Natural Gas. The first low sulfur fuel experiment was carried out firing natural gas in the 50-hp boiler. A single adsorbent sampler was operated simultaneously with a high-volume Method 5 sampling train. Following extraction and GC-MS analysis, the total POM loadings for each sampling system were calculated to

be: adsorbent sampler, $-1.3 \mu\text{g}/\text{m}^3$; high-volume Method 5, $-0.55 \mu\text{g}/\text{m}^3$.

Although the adsorbent sampler is still significantly more efficient than the impinger method, it is interesting to note that the discrepancy is considerably less than the greater than 10 to 1 ratios observed for relatively high sulfur residual oils; the adsorbent sampler in this case collected 2.4 times as much POM as the impinger method. A second low sulfur emission experiment was carried out at a carbon black manufacturing facility, as described subsequently.

Validation Experiments—Residual Oil with Variable Air Fuel Ratios. Figure 3 shows the results for POM, particulate, and Bacharach smoke plotted as a function of CO_2 for four air/fuel ratios. POM was collected simultaneously by two methods, the high-volume Method 5 impinger system and the adsorbent sampling system. The results are additionally presented in Table II.

The two systems show good agreement for particulate loading. However, the adsorbent sampler again appears to be a more effective collector of POM than the impinger-filter system, especially at the higher loading.

Analysis of POM Effluents from Carbon Black Manufacturing Facility. The adsorbent sampling system was further evaluated during an EPA-sponsored program to monitor the POM emissions from a carbon black manufacturing facility (13). In this experiment a standard EPA Method 5 sampling train was run with an adsorbent sampler backup, and a separate adsorbent sampler was run in parallel with this system. Other parameters measured at this facility showed that the sulfur oxide content of the stack gas was very low compared to the previous residual oil experiments reported above.

Following sample extraction and GC-MS analysis, the total POM loading of each part of the sampling system was calculated to be: EPA Method 5, $-56.5 \mu\text{g}/\text{m}^3$; adsorbent sampler backup to EPA Method 5, $-19.5 \mu\text{g}/\text{m}^3$; and adsorbent sampler, $-124 \mu\text{g}/\text{m}^3$.

The results of this study were almost comparable to results obtained from the 50-hp boiler firing natural gas. The ratio of efficiencies of the adsorbent sampler and Method 5 was lowered slightly to 2.2 compared to the natural gas experiment, but the backup adsorbent sampler loading was unable to account for the POM deficit from the Method 5 sampling train. It would appear that serious losses are still occurring in the Method 5 sampling system. The adsorbent sampler is again significantly more efficient than Method 5 regarding POM collection efficiency and sample recovery.

Conclusions

The adsorbent sampler provides an extremely simple sampling technique from the standpoint of operation and sample recovery when compared to EPA Method 5. Not only is the adsorbent sampler at least twice as efficient as the EPA Method 5 train in collecting POM, but utilization of the adsorbent sampler can reduce sample-recovery time as much as 50%. In addition, when burning higher sulfur fuels, the performance of the adsorbent sampler is far superior to that of the Method 5 train, especially when operating a combustion system at a relatively high particulate loading.

The value of the integral heat exchanger should not be overlooked. In addition to permitting use of the adsorbent sampler for a wide range of stack gas temperatures, condensation of water vapor may be obviated by operating the sampler at about 10°F or more above the dew point.

In future studies we propose to carry out a detailed study of the fate of sulfur oxides in the sampler. Additionally, validation for a wide range of organic species other than

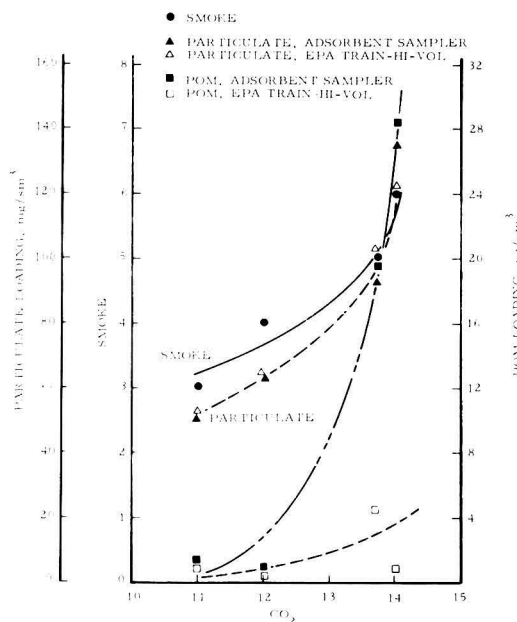


Figure 3. Particulate and POM vs. CO_2

Table II. Emissions from 50-hp Boiler as Measured with Two Sampling Trains

| | Boiler operating condition | | Particulate loading, mg/sm^3 | POM loading, $\mu\text{g}/\text{sm}^3$ |
|----------------------|----------------------------|-----------------|--|--|
| | CO_2 | Bacharach smoke | | |
| High-volume Method 5 | 11.0 | 3 | 52.1 | .55 |
| Adsorbent sampler | 11.0 | 3 | 50.3 | 1.46 |
| High-volume Method 5 | 12.0 | 4 | 63.2 | 1.01 |
| Adsorbent sampler | 12.0 | 4 | 63.0 | 1.03 |
| High-volume Method 5 | 13.7 | 5 | 92.8 | 4.37 |
| Adsorbent sampler | 13.7 | 5 | 102.3 | 19.4 |
| High-volume Method 5 | 14.0 | 6 | 135.0 | 0.79 |
| Adsorbent sampler | 14.0 | 6 | 122.1 | 28.6 |

POM will be carried out, in addition to a more detailed evaluation of optimum sampling temperatures.

It is strongly recommended that future POM sampling should be carried out by sampling systems similar to the Battelle-developed adsorbent sampler; its comparison with Method 5 throws serious doubts upon earlier data which were obtained by the latter method.

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Detection of Vinyl Chloride and Related Compounds by a Gas Chromatographic, Chemiluminescence Technique

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■ A new measurement technique for the detection of vinyl chloride is presented. This technique involves two phases: separation of vinyl chloride from other trace gases by use of a gas chromatographic column and detection of radiation resulting from the chemiluminescent reaction of ozone and vinyl chloride. A linear relationship between chemiluminescent response and concentration is obtained at parts per million levels with a noise equivalent concentration of 50 parts per billion. Commercially available chemiluminescence analyzers for the nitrogen oxides can be modified and interfaced with gas chromatographic equipment to speed commercial implementation. Sensitivity of the technique is sufficient to meet monitoring requirements imposed by recently established employee exposure standards.

The recent disclosures implying a causal relationship between exposure to vinyl chloride monomer (VCM) and angiosarcoma of the liver have resulted in a program of monitoring for VCM in industrial, home, and office environments. For the industrial environment, NIOSH (1) has established an exposure limit of 1.0 ppm averaged over any 8-h period and a ceiling of 5 ppm averaged over any period not exceeding 15 min. Initial monitoring and measurement are required to establish whether any employee is exposed to VCM in excess of 0.5 ppm averaged over an 8-h period. Subsequent schedules for monitoring are based on these initial findings. The method of monitoring and measurement must have an accuracy (95% confidence interval) of not less than $\pm 50\%$ from 0.25 through 0.5 ppm, $\pm 35\%$ from 0.5 through 1.0 ppm, and $\pm 25\%$ over 1.0 ppm. Surveys of residential areas adjacent to industrial sources of VCM are being carried out (2). Exposure levels in the home and office, as a result of using products which contain VCM as a propellant, are being measured [see, for example, Gay et al. (3)]. Concurrent with these programs for

monitoring, health effects research is being continued to more accurately define the threshold harm levels (4). Thus, many applications exist for reliable, sensitive instrumentation for VCM.

The most widely used technique for analysis of VCM is gas chromatographic separation followed by flame ionization detection (GC-FID). The sample to be analyzed is usually passed through a tube packed with activated charcoal or some other adsorbent. The accumulated sample is then desorbed for analysis. CS_2 extraction of VCM adsorbed on activated charcoal has been discussed recently by Cuddeback et al. (5) and is routinely used by NIOSH (6). Thermal desorption from Carbosieve B has been discussed by Russell (7). This paper explains the use of a chemiluminescence detector (CD) to replace the FID. The light emission from the products resulting from the gas-phase reaction of ozone and vinyl chloride provides the basis for detection. Since the CD responds to a smaller group of compounds than the FID, detection of VCM is made with more specificity. This promises to eliminate interference (resolution) problems which have been experienced in field tests with the GC-FID (8). Additional advantages which are evident from field use of similar commercial chemiluminescence monitors include simplicity of operation and low maintenance. Fewer support gases are required for CD, and the potentially hazardous use of H_2 is avoided.

Discussion

The bimolecular reactions between ozone and the olefinic hydrocarbons result in chemiluminescence from excited reaction products. One of the reactions, that between ozone and ethylene, is the basis for the current Federal Reference technique for monitoring ambient levels of ozone (9). In this application, ozone in an ambient air sample is mixed continuously with an excess of ethylene, and the resulting output is monitored on a closely coupled photomultiplier. By reversing the roles of the ethylene and ozone, trace concentrations of

ethylene can be detected. However, other olefins and substituted olefins in the ambient sample also produce light in the same spectral range. Kummer et al. (10) and Pitts et al. (11) have taken emission spectra of a number of hydrocarbon reactions and, based on the results, have classified olefins into three structural groups typified by ethylene, *cis*-2-butane, and isobutene. Finlayson et al. (12) have presented the kinetics and mechanisms operative in low-pressure ozone, olefin reactions. Emission from vibrationally excited OH ($\lambda > 550$ nm) and from HCHO ($350 < \lambda < 600$ nm) were common to all species examined while spectral differences form the basis for discrimination between structural groups. Quickert et al. (13) have demonstrated the feasibility of detecting substituted olefins by measuring light output from the reaction of ozone with C_2H_3Cl and C_2H_3F .

Experimental

The experimental arrangement used to monitor vinyl chloride is shown in Figure 1. The system was operated first without and later with the gas chromatographic column, alternate choices being indicated at position A of Figure 1. The cylindrical reaction chamber was Teflon lined, 1.9 cm in diameter and 1.9 cm in length. A small diameter Teflon (sample) tube and a concentric, larger diameter stainless steel tube (O_3 in O_2) were used to carry the reactants through the center of the chamber to be mixed immediately in front of a thermoelectrically cooled 4501 RCA photomultiplier. The chamber was vented from the end opposite the photomultiplier. No filters were placed between the photomultiplier and the reaction chamber so that the responses obtained represent the integrated product of tube sensitivity and chemiluminescence intensity.

An ozone generator obtained from a commercial NO_x monitor (Bendix, Model 8004) supplied approximately 2% ozone in an oxygen stream at a typical flow rate of 30 ml min^{-1} . The specific ozone concentration during studies of the effect of varying ozonizer flow was determined by monitoring the attenuation of 2537 \AA radiation from a low-pressure mercury discharge lamp (Ultraviolet Products, Inc.). The lamp was mounted on one side of a 1.0-cm quartz cell through which the ozonizer output was channeled. A 1P28 photomultiplier (RCA) filtered with a 2537 \AA interference filter and a 7-54 Corning glass filter were mounted on the opposite side of the quartz cell. Ozone concentrations were determined from the equation $\text{Log}_{10} I/I_0 = -a(O_3)l$ where I and I_0 are proportional to the 1P28 response with and without ozone in the cell, l denotes the cell width, and a denotes the ozone absorptivity. A value of $3280 \text{ cm}^2 \text{ mol}^{-1}$ corresponding to 273°C and 760 mm Hg was used for a (14).

A Chromatronic type CAV "Cheminert" valve with a three-way switching pattern and a manually controlled, pneumatically actuated switch facilitated sample injection to the gas chromatographic column. The column used was a 2.5-m section of 3.0 mm i.d. Teflon tube filled with 0.4% Carbowax 1500 on Carpack A (Supelco, Inc.). Modifications to the initial column design are explained later in the text. Column temperature was not controlled and remained near the average room temperature of 23°C . Nitrogen carrier gas was used throughout the tests. Vinyl chloride permeation tubes (Analytical Instrument Development) were gravimetrically calibrated on a Cahn electrobalance and placed in a constant temperature jacket. Known concentrations of vinyl chloride could be obtained by passing zero air at controlled flow rates over the permeation tube surface (15).

Two different sets of electronics were used. Signals from the photomultiplier were amplified with either a Keithley Model 417 picoammeter or the amplifier on a Meloy Model 0A350 ozone analyzer, and then traced on a Hewlett-Packard 17100B chart recorder. The Meloy electronics offered some advan-

tages in signal response by providing adjustable time constants.

Results

Without Gas Chromatographic Column. The detector system was initially evaluated without the GC column. A small pump (Metal Bellows Corp., Model MB-21) was used to evacuate the reaction cell; chamber pressure was near atmospheric. A set of Corning filters was employed to identify the spectral characteristics of vinyl chloride-ozone chemiluminescence. To do this, the signal intensity transmitted by each of the set of low wavelength cutoff filters was recorded. A curve of intensity vs. wavelength values for 50% attenuation, i.e., wavelength values taken from Corning's spectral transmission curves, was drawn. The first derivative of this curve was an approximation to the spectral distribution of chemiluminescence. The spectral distribution was essentially identical to that reported for the ethylene, ozone reaction (10) over the interval 250–650 nm.

Response to other unsaturated compounds was measured to estimate the extent of interference. The response curves for several compounds as a function of concentration are shown in Figure 2. Samples were made by volumetric dilution in Tedlar bags. Since the bags were used almost immediately, sample losses (16) were minimized. Sample flow rate and flow

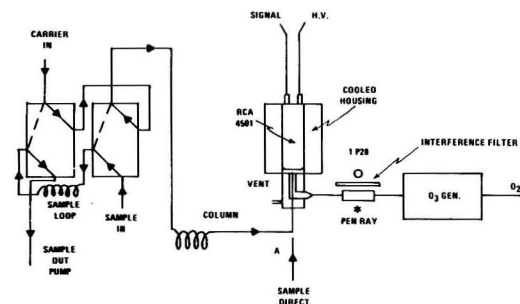


Figure 1. Experimental arrangement for vinyl chloride detection. Chromatographic column attached at position A

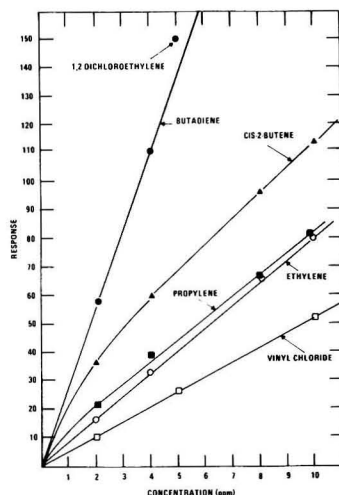


Figure 2. Hydrocarbon response vs. concentration for unsaturated compounds

rate through the ozonizer were both set at 30 ml min^{-1} . The response curves are similar to those obtained by Quickert et al. (13) in their studies of ozone, hydrocarbon chemiluminescence. In both studies the response is linear with concentration except for slight nonlinearities for propylene and *cis*-2-butene. Relative responses for a given concentration of different hydrocarbons are also roughly the same in the two sets of data. In general, the hydrocarbons with higher rates of reaction with ozone give the greatest response.

With Gas Chromatograph. To isolate vinyl chloride, a gas chromatographic column was coupled to the reaction chamber, and samples were run using a carrier gas flow rate of 30 ml min^{-1} and a 10-ml sample loop. Both the sample and ozonizer flow rates were established by pushing air through the reaction chamber. Figure 3 (solid lines) shows complete baseline separation for the vinyl chloride peak using a sample containing ethylene, propylene, isobutylene, *cis*-2-butene, 1,3-butadiene, and 1,2-dichloroethylene in addition to vinyl chloride. Further tests have shown that 1-butene (dotted lines in Figure 3) is well separated from vinyl chloride. The initial column was later replaced with one of 6.7-m length and a 25-ml sample loop. With a carrier gas flow rate of 30 ml min^{-1} , the noise equivalent concentration (NEC) based on peak height was 50 ppb. Peak height was linear with concentration from the NEC to 10 ppm. Baseline separation was maintained with the new column.

Comparison Between Experimental Results and Theoretical Model. In the experimental arrangement used to obtain the chromatogram shown in Figure 2, the residence time of the sample in the reaction cell (5.4 s for a 60 ml min^{-1} total flow rate and a cell volume of 5.4 ml) is short compared to the peak width for VCM (40 s). In addition, the peak width at half maximum points is approximately the same as the time required to deposit VCM on the column. In this case, the signal response at the VCM peak is approximately the same as the response from a system without the gas chromatographic column, i.e., the VCM concentration in the cell during peak response is approximately the same as that obtained when sampling directly. Provided these conditions hold, a theoretical model developed for a system without a column will also apply when a column is used. Some minor differences are expected due to the use of N_2 instead of air as a carrier for VCM (12) and because distribution of VCM in the carrier is shaped during passage through the column. To compare experimental and theoretical results, ethylene was used instead of vinyl chloride since the reaction rate for the ozone, ethylene reaction is accurately known [see, for example, Herron and Huie (17)]. Conclusions based on this comparison also apply to the VCM, ozone reaction.

Variation of system response with system parameters can be explained by reference to work by Steffenson and Stedman (18). They analyze the functional dependence of response to system parameters for the bimolecular reaction between NO and O_3 . In the present case, a treatment of the $\text{C}_2\text{H}_3\text{Cl}(\text{C}_2\text{H}_4)$ and O_3 reaction can be considered analogous if the light-producing compounds are quenched in bimolecular collisions. Equation 10 of ref. 18 then gives the correct form for the photomultiplier response:

$$\text{Signal} \sim (cF_s G/P) [1 - \exp(-C(\% \text{O}_3)F_m/(F_m + F_s)^2)] \quad (1)$$

in which c denotes $\text{C}_2\text{H}_3\text{Cl}(\text{C}_2\text{H}_4)$ concentration in atmospheres, F_s and F_m denote sample and ozonizer flow rates, respectively, $\% \text{O}_3$ denotes the percentage O_3 in the ozonizer stream, G denotes a geometrical term related to the spatial distribution of chemiluminescence, and C denotes the product $V P^2 k_t$ where V corresponds to the reaction chamber volume, P the reaction chamber pressure, and k_t the total reaction rate between ozone and ethylene. Experimental (dotted line) and predicted values based on Equation 1 are shown in Figure 4.

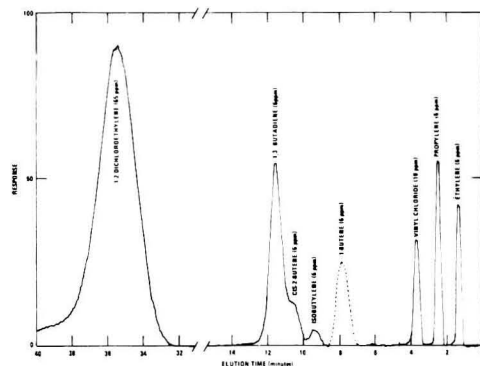


Figure 3. Chromatogram showing vinyl chloride separation
Conditions: column, $2.5 \text{ m} \times 3 \text{ mm}$ packed with 0.4% Carbowax 1500 on Carbowax A; temperature, 23°C ; ozonator flow of $30 \text{ ml min}^{-1} \text{O}_2$; carrier gas flow of $30 \text{ ml min}^{-1} \text{N}_2$; sample size 10 ml

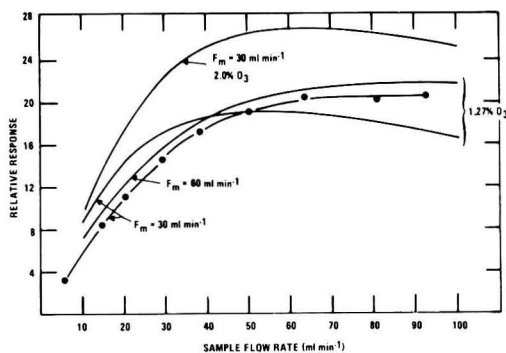


Figure 4. Parameter study of chemiluminescent response as function of sample flow rate
Reactants: O_3 and $\text{C}_2\text{H}_3\text{Cl}$; solid dots indicate experimental points

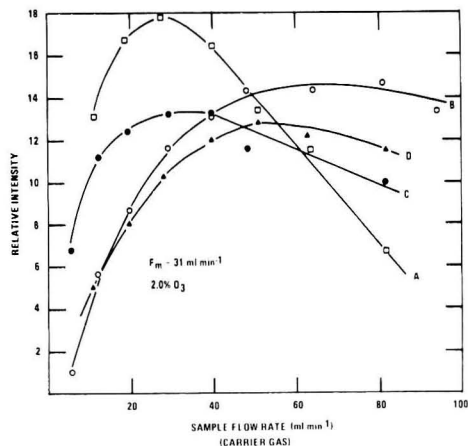


Figure 5. Chemiluminescent response for C_2H_4 and $\text{C}_2\text{H}_3\text{Cl}$ with O_3
Curve A: $\text{C}_2\text{H}_3\text{Cl}$ without column; Curve B: C_2H_4 without column; Curve C: $\text{C}_2\text{H}_3\text{Cl}$ with column; Curve D: C_2H_4 with column; $2\% \text{O}_3$; Curves A and C multiplied by factor of 2.8 for convenience of display

In the calculation of predicted values, the factor G is considered constant. Experimental values are normalized to the value of signal response calculated for the optimum sample flow rate, F_s^* . The value of F_s^* is obtained by setting the derivative of the signal response, S , with respect to sample flow rate, F_s , equal to zero and solving for F_s . For the conditions, $k_t = 5.62 \times 10^5 \text{ ml mol}^{-1} \text{ s}$ (17) at atmospheric pressure, $F_m = 30 \text{ ml min}^{-1}$, % $\text{O}_3 = 1.27$, the value of $F_s^* = 50 \text{ ml min}^{-1}$, and the experimental and theoretical curves are made to cross at this point.

The signal response is roughly linear as a function of sample flow rate for low flow rates. As F_s is increased, the reaction between ozone and ethylene does not have sufficient time to go to completion before the mixture is swept out of the reaction cell. When this happens, the rate of response is less than linear, i.e., the last term in Equation 1 becomes important. Differences in the experimental and predicted shape of response curves are attributed to nonuniformity of mixing and to the assumption of a constant value for G . Figure 5 shows the comparison between response characteristics obtained with and without a column (10-ml sample loop and 2.5-m column) for both vinyl chloride (Curve A without, Curve C with) and ethylene (Curve B without, Curve D with). Curves A and C are multiplied by a factor of 2.8 to facilitate plotting. Peak height values were plotted for Curves C and D. Experimental conditions were $F_m = 31 \text{ ml min}^{-1}$, % $\text{O}_3 = 2\%$ and F_s variable. Sample concentrations of 10 ppm were used for both ethylene and vinyl chloride. Maximum response for the two gases occurs for different carrier gas flow rates, reflecting a higher reaction rate between ethylene and ozone. Due to the higher reaction rate, the response characteristic for C_2H_4 remains approximately linear for a greater range of F_s . By comparing Curves A and B (without column) to C and D (with column), it is obvious that the value of F_s for which optimum response occurs is about the same with and without the column, as assumed earlier. Peak height response for VCM is only 0.8 of the value without a column due to sample shaping on the column.

Repeated measurements of the same sample have indicated that a variation in peak height response of 2% about the mean value can be expected. Comparisons were made between the laboratory prototype system and a Perkin-Elmer 900 gas chromatograph with a flame ionization detector. Although the sensitivity achieved with the FID was greater for the same column conditions, the expected enhancement of specificity with the GC-CD was evident. Further enhancement of sensitivity for the GC-CD is anticipated by reduction of reaction chamber pressure and more efficient collection of light from the VCM, O_3 reaction.

Conclusions

The combination of chemiluminescence detection and gas chromatographic separation has made possible specific and sensitive monitoring of vinyl chloride. A noise equivalent concentration of 0.05 ppm without preconcentration indicates that ambient surveying near vinyl chloride sources is feasible. Commercial NO_x analyzers based on chemiluminescence use a detector configuration and ozonizer similar to those used in

the present work. Hence, commercial implementation of the detection scheme for vinyl chloride is feasible with the addition of a gas chromatographic column and suitable design modifications. The sensitivity and precision of the technique are sufficient to meet the requirements for establishing compliance with the recently announced exposure standards (1). The use of chemiluminescence as a detection technique for gas chromatographic columns also promises a solution to interference effects between saturated and unsaturated higher molecular weight organics since the saturated compounds do not cause a chemiluminescence response. The simple model used in this work provided useful information and insight into the response characteristics of the chemiluminescence detection system.

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Feasibility of Oil Slick Removal from Seawater Using Power Lasers

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■ A high-power-cw CO₂ laser was used to investigate, in the laboratory, the conditions for the evaporation and decomposition and burning of crude oil from water surface. The range of activation energies for decomposition of crude oil (80% of it) on water surface is estimated to be from 1–10 kJ.g⁻¹, and requires about 25 times higher beam intensities (at least 200 W.cm⁻², but preferably > 1 kW.cm⁻²), than that for evaporation. On the basis of these data, the performance of a projected shipborne 100–500-kW laser head, powered by either a conventional generator or atomic reactor, may become competitive with Filter-belt (“Spill Spoiler”) or Foam-belt separators, if the overall efficiency of the laser exceeds 25%. It also became evident that pulsed operation will offer distinct advantages for beam control and efficiency.

It is estimated that oil is produced now at a rate of 2×10^{15} gal per year (1). Less than 1 ppm of it (about 1.9×10^9 gal) is spilled on water from various sources, causing ever-increasing pollution problems. The relative contributions from these sources are (2, 3): transportation and terminal operation, 35%; river and urban runoff, 31%; atmospheric fallout and natural seeps, 20%; coastal refineries and industrial waste, 13%; offshore oil production, 1%.

The current techniques of oil slick removal are (4, 5): skimming it off the surface using “Filter Belt” (Martin-Marietta), “Foam Belt” (Br. Petroleum Trading Ltd.), floats, suction devices and separators, all of which are claimed to recover 90% of oil trapped in containment booms; burning and decomposing the oil; adsorbing and absorbing it into straw, plastic foam chips, and so forth; converting it into gell which is much easier to collect; sinking it by spraying with suitable chemicals; emulsifying and dispersing it (6); consuming it with various bacteria; photooxidizing it using photosensitizing agents, or employing several other less practical methods.

The most important factors in using any of these techniques are their economy, speed, environmental safety, and convenience. Although economy may not be decisive in environmental emergency situations, speed of removal is. In this sense a feasibility study of oil slick removal by means of ir-power lasers was undertaken on a limited scale in this laboratory, with preliminary results reported here in order to assess the merits of a proposed shipborne laser head.

Physical Properties of Oil Slicks

The crude oil consists mainly of liquids of the paraffin series C₅H₁₂ to C₁₆H₃₄ and solids from C₁₇H₃₆ to C₄₅H₉₂, with small amounts of other compounds depending on the origin of the oil (5).

It is known that after 12 h of the initial oil spill at sea about 18%, by weight, almost all light components of crude oil (Kuwait) have evaporated (5). In 24 h this loss reaches 20%, and thereafter the residue disperses only slowly. The residue consists mainly of hydrocarbons containing C₁₄ to C₄₅ (5). The heat of evaporation of 80% of this residue is typically from 0.5–1 kJ.g⁻¹ (0.5×10^9 J.ton⁻¹). The activation energy for decomposition of the lighter fraction of the residue is given elsewhere (7, 8), but the given value becomes lower in the

presence of oxygen. Its effective value, accounting for losses in water and scattering, is estimated in our experiments to be 1–10 kJ.g⁻¹ ($2 - 10 \times 10^9$ J.ton⁻¹), varying widely with the effective absorption of laser beam energy in the oil layer, in dependence of its thickness.

One m³ of crude oil (Kuwait) spreads in 10 min, typically (5) over an area of about 2×10^3 m², varying in thickness from 0.1 to > 1 mm. After 24 h the thickness is typically from 1–2 μm, which corresponds to 1200–2400 l.km⁻², averaging in weight 2 tons.km⁻². However, in contaminated water, the oil film thickness may stay, in the central area, between 1 and 3 mm. Thus, the laser evaporation technique was tested on oil films between these limits in conjunction with several known collection techniques, such as the electrostatic precipitation and separation by suction filtering.

To evaporate a 1-mm thick oil film on water, a laser beam (CO₂) intensity of 40 W.cm⁻², at least, but preferably >100 W.cm⁻² is necessary. Consequently, for a proposed laser scanning head of 5×0.05 m² working area (at 10-m distance from the exit), a total beam power from 100–250 kW is required, depending on the “sweeping” speed.

Experimental Data

The laboratory experiments initially involved a 125-W-cw CO₂ laser of 1-m cavity, operating at multimode between 20 and 25% efficiency. These experiments did not account for wind, waves, or seawater contamination.

First, it was difficult to avoid the co-evaporation of a lot of water when evaporating a thin film of oil. Although water vapor exhibits a wide transmission “window” for wavelengths from 8–13 μm to enable the beam to penetrate the cloud, nevertheless the energy loss due to large heat of evaporation of water (2.3 kJ.g⁻¹) will be prohibitive—unless the laser beam is switched on and off by an oil-and-water-vapor-sensing device. The already established ir, microwave and UV fluorescence oil-sensing techniques can be adapted for this purpose (9–14).

Also, it must be considered, that water vapor behaves as a saturable absorber for high-energy CO₂ laser pulses (15). Of course, the evaporation of oil assumes an effective collection and separation, either by electrostatic or suction techniques, both of which were attempted qualitatively only.

On the other hand, for the decomposition and burning of heavy oil on water surface, a laser beam intensity > 200 W.cm⁻² and energy from 2–10 kJ.g⁻¹ is required, both varying with the thickness and composition of oil film. Evidently, oil on water in a thickness less than 3 mm would not burn steadily (5), but decomposes in miniexplosions.

Conclusions

If we assume the price of shipborne electricity, tentatively, at \$4.00 for 1000 kWh and a 25% laser efficiency, the energy cost of evaporating oil from a water surface would amount to \$2.2 to \$18 per ton, not accounting for overhead.

A 100-kW laser head can be accommodated on a relatively small (<100 ft long) water craft. The ship and her crew can be easily protected from reflected beams by using suitable ir-absorbing materials. However, a further study is required to evaluate the reach and the effects of outward scattering.

At the present state of the art, only CO₂, CO, and some chemical lasers of the hydrogen-halogen variety are capable of the above indicated efficiency and output (16–18).

Of the cw CO₂ industrial lasers, the sealed types are limited to outputs of a few hundred watts. The axial flow lasers of folded and multistage construction are acceptable, preferably those having a recirculating system in which a catalyst (or a heater) reverses the disassociation reaction in the gas mixture.

The transversely excited atmospheric (TEA) pressure, pulsed CO₂ lasers, employing preionization, seem to have the advantage of easier beam switching control by the oil-sensing devices mentioned earlier, which will improve the economy of oil recovery considerably. Whether this economy becomes comparable to that of the catamaran Spill Spoiler (*Offshore*, Sept. 1974) with its belt pick-up capacity of 2000 gal/min, cannot be reliably predicted from our limited study.

Speculatively, a larger nuclear-powered laser head, employing a nuclear reactor for power, or a direct nuclear laser (19) (e.g., He-Xe, Ne-N₂ a.o.) capable of operating over long periods at open sea, may have the potential of becoming an oceans' cleanup instrument of some joint international authority.

Finally, it is recognized that the technical problems of oil and water vapor separation and laser efficiency, one of the main objects of our study, require further investigation before all engineering aspects of this concept can be completed.

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Preparation of Homogeneous Dust Sample for Comparison of Analytical Results of Atmospheric Samples

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■ A simple procedure for the preparation of homogeneous dust samples which are useful for comparing the analytical results of atmospheric samples is proposed. The homogeneity of the sample is examined by statistical treatment of the analytical data; the variances due to analytical errors and inhomogeneity of the samples are compared by the *F*-test. The homogeneous sample thus prepared is distributed to six laboratories and analyzed by neutron activation analysis, atomic absorption spectrometry, and x-ray fluorescence spectrometry for 38 elements. Relative standard deviations of the results of interlaboratory analyses of neutron activation analysis are less than 25% for 16 elements at μg levels.

The international standard reference materials are useful to evaluate new analytical procedures and to compare the analytical results obtained by different analysts or laboratories. The geological powder samples distributed throughout the world by the U.S. Geological Survey are useful to analytical chemists for these purposes. However, standard samples for studies of airborne particulate matter are not yet available. In this paper the possibility of the preparation of a uniform powder sample is indicated, together with the method of preparation. The method is simple and can be applied to the preparation of dust samples from any kind of airborne particulate matter for comparison of the results of elemental analysis.

We have searched for a large source of dust whose composition is similar to the airborne particulate matter. For this purpose, the dust collected on an air filter made of cloth was chosen. The filtering cloth is attached to the air conditioning equipment installed on the roof of an office building in the business district.

A size distribution study made with the Andersen impactor reveals that the main aerodynamic size of the dust powder is approximately 4 μm , and most of the fraction smaller than 1 μm in size, which can be harmful to human health, is lost during the air sampling process. Although the present sampling technique is not ideally suited to elemental determination of dust samples of submicron ranges, it has, however, an advantage in that it allows collection of powder samples that approximate in chemical composition airborne particulate matter. Both biological and geochemical standard materials fail to provide similar constituents to the airborne particulate matter in terms of carbonaceous and halide components.

In addition, the present sampling technique can provide several kilograms of dust samples in comparison with several hundred milligrams that can be obtained in 24 h with a high-volume air sampler.

Experimental

Preparation of Homogeneous Sample (AS-1). About 6 kg of the dust was collected by a household vacuum cleaner on a cloth filter attached to an air inlet of an air conditioning unit, which was placed on the roof of an office building some 50 m high. The collected dust was carried to our laboratory in a polyethylene bag. Two kg of the dust was dried in an oven at $105 \pm 5^\circ\text{C}$ for 1 h and sieved through the standard sieves of 50, 100, and 200 mesh. The dust which passed through the 200-mesh sieve was again dried in an oven under the same conditions for about 1 h, by leveling the dust powder in a vat to about 1-cm thickness.

The dried powder was put into a 5-l. polyethylene bottle with a large mouth and was mixed by rotating the bottle with the stirring bodies in it: one hundred 25-mm ϕ balls of 34 g each, and twenty 25 mm ϕ \times 25 mm cylinders of 22.5 g each, both covered with polyurethane film.

The degree of mixing was examined by chemical analysis of six aliquots of each sample taken from the body before mixing and after 3 and 6 h of mixing. The coefficients of variation of the analytical data for zinc in the samples were 4, 3, and 1–2%, respectively, and no improvement of coefficient was seen for the samples mixed longer than 6 h. Thus, a stirring time of 10 h was chosen for the sample mixing.

For further mixing, the powder was divided into two equal parts by a riffle sampler ("Book of ASTM Standards with Related Materials", Part 19, p 17, 1967); half of one pile was spread in a large vat, and half of the other pile was also spread over the former. By repetition of this procedure, the mixed powder processed by the riffle sampler at one time forms four layers in a vat. The surface of the layer is marked off by straight lines into 16 rectangles to take out the 16 equal four-layer parts. The powder thus processed is divided into 64 parts ($4 \times 16 = 64$). If this procedure is repeated four times by passing the 16 parts successively through the riffle sampler in a random order, the powder is divided into $64^4 = 1.7 \times 10^7$ parts theoretically. Since the weight of the initial dust powder was 1 kg, one single division by this procedure is about 60 μg . Now the whole dust sample can be regarded as homogeneous.

The standard sample thus prepared was named AS-1 for convenience and was statistically examined for its homogeneity by the data obtained by chemical analysis of the sample.

Dissolution Procedure for Chemical Analysis. One hundred mg of AS-1 was first extracted in a 250-ml Erlenmeyer flask with a reflux condenser with nitric acid (1 + 1) by direct heating for 30 min. Three ml of hydrogen peroxide was

Table I. Analytical Results of Aliquots of Series A by Atomic Absorption Spectrometry ($\mu\text{g/g}$)

| No. of aliquot | Element | | | |
|--------------------------------|------------------------|--------------------------|------------------------|-----------------------------|
| | Zinc ($\times 10^3$) | Copper ($\times 10^2$) | Lead ($\times 10^3$) | Manganese ($\times 10^3$) |
| x_1 | 3.13 | 3.5 | 2.6 | 1.07 |
| x_2 | 3.11 | 3.4 | 2.6 | 1.06 |
| x_3 | 3.10 | 3.3 | 2.7 | 1.09 |
| x_4 | 3.05 | 3.4 | 2.6 | 1.08 |
| x_5 | 3.09 | 3.6 | 2.6 | 1.10 |
| x_6 | 3.03 | 3.4 | 2.6 | 1.08 |
| x_7 | 2.96 | 3.3 | 2.6 | 1.08 |
| x_8 | 2.97 | 3.5 | 2.8 | 1.06 |
| x_9 | 2.98 | 3.5 | 2.6 | 1.10 |
| x_{10} | 3.00 | 3.4 | 2.7 | 1.09 |
| \bar{x} | 3.04 | 3.4 | 2.6 | 1.08 |
| $V_{\text{anal}+\text{mix}}^a$ | 3970 | 90 | 4900 | 210 |
| cv, % | 2.1 | 2.8 | 2.6 | 1.3 |

$$^a v = \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2 / (n-1).$$

Table II. Analytical Results of Aliquots of Series B by Atomic Absorption Spectrometry ($\mu\text{g/g}$)

| No. of aliquot | Element | | | |
|---------------------|------------------------|--------------------------|------------------------|-----------------------------|
| | Zinc ($\times 10^3$) | Copper ($\times 10^2$) | Lead ($\times 10^3$) | Manganese ($\times 10^3$) |
| x_{11} | 3.06 | 3.7 ₄ | 2.5 ₆ | 1.11 |
| x_{12} | 3.10 | 3.7 ₆ | 2.6 ₆ | 1.10 |
| x_{21} | 3.05 | 3.7 ₄ | 2.6 ₅ | 1.10 |
| x_{22} | 3.15 | 3.6 ₂ | 2.5 ₆ | 1.09 |
| x_{31} | 3.11 | 3.5 ₅ | 2.5 ₆ | 1.09 |
| x_{32} | 3.02 | 3.4 ₈ | 2.5 ₈ | 1.10 |
| x_{41} | 3.01 | 3.4 ₄ | 2.7 ₁ | 1.10 |
| x_{42} | 2.96 | 3.6 ₁ | 2.6 ₄ | 1.10 |
| x_{51} | 3.02 | 3.4 ₇ | 2.5 ₉ | 1.11 |
| x_{52} | 2.97 | 3.4 ₄ | 2.6 ₂ | 1.10 |
| x_{61} | 2.99 | 3.3 ₄ | 2.5 ₈ | 1.08 |
| x_{62} | 3.01 | 3.3 ₅ | 2.6 ₂ | 1.08 |
| x_{71} | 3.01 | 3.5 ₅ | 2.5 ₇ | 1.11 |
| x_{72} | 2.97 | 3.4 ₈ | 2.5 ₉ | 1.10 |
| x_{81} | 3.07 | 3.4 ₈ | 2.6 ₂ | 1.10 |
| x_{82} | 2.94 | 3.4 ₈ | 2.6 ₂ | 1.08 |
| x_{91} | 2.94 | 3.5 ₉ | 2.5 ₉ | 1.09 |
| x_{92} | 2.99 | 3.3 ₅ | 2.5 ₈ | 1.10 |
| x_{101} | 3.04 | 3.4 ₆ | 2.7 ₁ | 1.06 |
| x_{102} | 3.01 | 3.4 ₇ | 2.5 ₉ | 1.07 |
| \bar{R}^a | 0.06 | 0.08 | 0.05 | 0.09 |
| V_{anal}^b | 2680 | 48 | 1800 | 60 |
| cv, % | 1.7 | 2.0 | 1.6 | 0.7 |

$$^a \bar{R} = \sum_{i=1}^n |x_{i1} - x_{i2}| / n. \quad ^b \sqrt{V} = \bar{R}/c, \text{ where } c = 1.16.$$

Table III. Analysis of Variances for Atomic Absorption Data

| Element | $V_{\text{anal}+\text{mix}}$ | V_{anal} | Variance ratio, F^a |
|-----------|------------------------------|-------------------|-----------------------|
| Zinc | 3970 | 2680 | 1.48 |
| Copper | 90 | 48 | 1.9 |
| Lead | 4900 | 1800 | 2.7 |
| Manganese | 210 | 60 | 3.5 |

$$^a F_{0.05}^0(0.05) = 3.18, F_{0.01}^0(0.01) = 5.35.$$

added, and this mixture was heated 30 min. The residue was filtered off from the extract through a filter paper (No. 5C, Toyo Roshi Co.) and filled up with water to a mark in a 100-ml volumetric flask. The solution was then analyzed by atomic absorption spectrometry by use of the Varian-Techtron AA-5 instrument.

Owing to the hygroscopic property of the AS-1, it must be kept in a controlled atmosphere of 50% humidity at 25 °C, at least for 24 h before weighing. This can be done in a desiccator whose atmosphere is equilibrated with 43.2 wt % of sulfuric acid at 25 °C. The AS-1, dried in a desiccator with silica gel as the desiccating agent, increases in weight by 5% in 20 h when it is taken out into an atmosphere of 50% humidity.

Table IV. Analytical Results of AS-1 (Individual Aliquot) by Instrumental Neutron Activation Analysis^a (μg/g)

| No. of aliquot | Element | | |
|------------------------------------|------------------------------|------------------------------|------------------------------|
| | Aluminum (×10 ⁴) | Chlorine (×10 ⁴) | Vanadium (×10 ³) |
| x ₁ | 5.14 | 3.56 | 2.9 |
| x ₂ | 5.58 | 3.42 | 2.9 |
| x ₃ | 5.45 | 3.15 | 2.9 |
| x ₄ | 5.48 | 3.21 | 3.0 |
| x ₅ | 5.60 | 3.31 | 2.7 |
| x ₆ | 5.73 | 3.31 | 3.0 |
| x ₇ | 5.66 | 3.42 | 3.0 |
| x ₈ | 5.67 | 3.26 | 2.8 |
| x ₉ | 5.79 | 3.32 | 3.1 |
| x ₁₀ | 5.56 | 3.12 | 3.0 |
| \bar{x} | 5.57 | 3.31 | 2.9 |
| V _{anal+mix} ^b | 3.34 × 10 ⁴ | 1.79 × 10 ⁴ | 134 |
| cv, % | 3.3 | 4.0 | 4.0 |

$$^a \text{Mamuro (1). } ^b V = \sum_{i=1}^n (x_i - \bar{x})^2 / (n - 1).$$

Table V. Analytical Results of AS-1 (Repeated Analysis of One Aliquot) by Instrumental Neutron Activation Analysis^a (μg/g)

| No. of analysis | Element | | |
|--------------------------------|------------------------------|------------------------------|------------------------------|
| | Aluminum (×10 ⁴) | Chlorine (×10 ⁴) | Vanadium (×10 ³) |
| x ₁ | 5.74 | 3.34 | 2.8 |
| x ₂ | 5.49 | 3.29 | 2.8 |
| x ₃ | 5.36 | 3.40 | 2.8 |
| x ₄ | 5.39 | 3.35 | 3.0 |
| x ₅ | 5.44 | 3.49 | 3.0 |
| \bar{x} | 5.48 | 3.37 | 2.9 |
| V _{anal} ^b | 2.29 × 10 ⁴ | 5.73 × 10 ³ | 120 |
| cv, % | 2.8 | 2.4 | 3.8 |

$$^a \text{Mamuro (1). } ^b V = \sum_{i=1}^n (x_i - \bar{x})^2 / (n - 1).$$

Table VI. Analysis of Variances for Data of Instrumental Neutron Activation Analysis^a

| Element | V _{anal+mix} | V _{anal} | Variance ratio, F ^b |
|----------|------------------------|------------------------|--------------------------------|
| Aluminum | 3.34 × 10 ⁴ | 2.29 × 10 ⁴ | 1.5 |
| Chlorine | 1.79 × 10 ⁴ | 5.73 × 10 ³ | 3.1 |
| Vanadium | 134 | 120 | 1.1 |

$$^a \text{Mamuro (1). } ^b F_4^0(0.05) = 6.00.$$

Sampling Procedure of AS-1 for Statistical Evaluation.

Two series, A and B, of samplings of the aliquots from the mixture were made for statistical evaluation of AS-1. In series A the 100-mg aliquots were taken randomly from the whole sample, whereas series B consisted of the pairs of 100-mg aliquots taken from 0.3 g of the "very carefully mixed" sample; the 0.3-g part of AS-1 was taken by the same procedure as in series A and was mixed again for 3 min thoroughly by a vibrational mixer (Spex mixer-mill, No. 5100).

Results and Discussion

An evaluation of the uniformity of the sample was made by a comparison of the variance of analytical and mixing errors, V_{anal+mix}, and the variance of analytical errors, V_{anal}, of the analytical data of the sample. The sample is regarded as statistically uniform when the F value becomes unity, since there is no significant difference between the two variances questioned, which also means no increase of analytical errors due to inhomogeneity of the samples.

$$F = V_{\text{anal+mix}} / V_{\text{anal}} \quad (1)$$

If we assume the aliquots of series B are mixed thoroughly and errors of analysis are the same for both series, the difference in the errors between A and B series will show the uniformity of the mother body. For this comparison the principle of analysis of variance (Equation 1) was applied, in which F values of the analytical data were compared with F₂₂^α(α) from Fisher's distribution table at significance level, α, and degrees of freedom of θ1 and θ2. Hypothesis H₀, which predicts no significant difference present between V_{anal+mix} and V_{anal}, is evaluated by the following criteria:

Hypothesis H₀ is accepted if $F \leq F_{22}^{\alpha}(\alpha)$.

Hypothesis H₀ is rejected if $F > F_{22}^{\alpha}(\alpha)$.

The analytical data of series A aliquots are shown in Table I. The coefficients of variation of the analytical results of zinc, copper, lead, and manganese are 2.1, 2.8, 2.6, and 1.3%, respectively, and variance V_{anal+mix} is shown at the second line from the bottom. Analytical results, coefficients of variation, and variances of the aliquots of series B are shown in Table II.

The F values of each element calculated from the analytical data are shown in Table III; those of zinc, copper, lead, and manganese are 1.5, 1.9, 2.7, and 3.5, respectively. F₉^{0.05} cited from the F distribution table is 3.18 for 5% significance level; therefore, the hypothesis H₀ is accepted for zinc, copper, and lead. The F value of 3.5 for manganese is rejected as it slightly exceeds 3.18, but it is accepted for 1% significance level F₉^{0.01} = 5.35.

Therefore, the homogeneity of the AS-1 sample has been proved by statistical treatment of the analytical results by atomic absorption spectrometry.

Homogeneity of the AS-1 sample was also examined by instrumental neutron activation analysis at the Radiation Center of Osaka Prefecture (1). The analytical data for 10 individual aliquots and those of five repeated determinations of single aliquots are shown in Tables IV and V, respectively; in the latter case, errors caused by the sampling procedure were not included in the results since nondestructive analysis was used. With these data, F values of aluminum, chlorine, and vanadium are 1.5, 3.1, and 1.1, respectively, all of which are smaller than 6.00 for F₄^{0.05}, in accordance with hypothesis H₀, i.e., statistical homogeneity (Table VI).

The AS-1 sample thus prepared was distributed to several laboratories for comparison of the analytical data. The results are shown in Table VII (2).

The results for neutron activation analysis at four laboratories are listed together with the results by x-ray fluorescence and atomic absorption spectrometry. The data of activation

Table VII. Results of Interlaboratory Analysis of AS-1 ($\mu\text{g/g}$)^a

| Element | Analytical method and no. of detn | | | | | | |
|---------|-----------------------------------|-------------------------|-----------------------|------------------------|----------|------------------------|-----------------------|
| | INAA ^b 6 | INAA ^c 10 | NAA ^d 4 | INAA ^e 5 | XF/ 1 | AAS ^e 10 | AAS ^f 5 |
| Ag | 3 | 3.7 | | | | | |
| Al | 38000 | 55000 | 56000 | 49000 | | | |
| As | 60 | 43 | | 27 | | | |
| Au | 0.09 | | 0.42 | 0.4 | | | |
| Ba | | 680 | | 140 | | | |
| Br | 350 | 350 | | 330 | | | |
| Ca | | 63000 | 56000 | 50000 | | | |
| Cd | | | | | | 19 | 19 |
| Ce | | 33 | | 26 | | | |
| Cl | | 33000 | 34000 | 26000 | | | |
| Co | 23 | 30 | 30 | 22 | | | |
| Cr | 370 | 360 | 330 | 360 | 300 | | |
| Cs | 3.8 | 4.1 | | | | | |
| Cu | | 600 | | 320 | 2100 | 340 | 320 |
| Eu | | 0.79 | | 0.77 | | | |
| Fe | 47000 | 48000 | 39000 | 45000 | 47000 | 43500 | 44400 |
| Ga | | | | 13 | | | |
| Hf | 3.3 | 3.4 | | | | | |
| Hg | 9 | | | | | | |
| K | | 9700 | | 9600 | | | |
| La | 21 | 17 | | 16 | | | |
| Lu | | 0.3 | | | | | |
| Mg | | 15000 | 16000 | 19000 | | | |
| Mn | 1200 | 1300 | 1300 | 1300 | 900 | 1080 | |
| Na | 12000 | 15000 | 13000 | 14000 | | | |
| Ni | | 250 | | 210 | | | |
| Pb | | | | | 1800 | 2640 | 2030 |
| Rb | | 45 | | | | | |
| Sb | 39 | 44 | 29 | 43 | | | |
| Sc | 12 | 8.6 | 12 | 10 | | | |
| Se | 2 | | 16 | 10 | | | |
| Sm | 3.2 | 3.6 | | | | | |
| Ta | | 1.2 | | | | | |
| Th | 3.9 | 6.2 | | | | | |
| Ti | | 5800 | 4500 | 3700 | 2900 | | |
| V | 200 | 290 | 240 | 240 | 100 | 300 | |
| W | 3.2 | 28 | | 33 | | | |
| Zn | 2800 | 3800 | 4100 | 3500 | | 3040 | |

^aINAA: instrumental neutron activation analysis, NAA: neutron activation analysis, XF: x-ray fluorescence analysis, AAS: atomic absorption spectrometry. ^bJapan Atomic Energy Research Institute. ^cRadiation Center of Osaka Prefecture. ^dAtomic Energy Research Institute, Rikkyo University. ^eFaculty of Engineering, Keio University. ^fKanagawa Prefecture Environmental Center. ^gJapan Environmental Sanitation Center.

analysis were processed by computer systems at three of four laboratories. The results with activation analysis seem to be acceptable as microanalytical data with the exception of tungsten; relative standard deviations of the results were less than 25% for 16 elements (Al, Br, Ca, Cl, Co, Cr, Fe, La, Mg, Mn, Na, Sb, Sc, Ti, V, Zn) which were analyzed in at least more than three laboratories. The quantities of the elements analyzed are mostly at the microgram levels, since all of the aliquots taken were less than about 10 mg.

The data by x-ray fluorescence are based on a single measurement. Although the analytical data obtained by x-ray fluorescence spectrometry are in good agreement with those by other analytical techniques, copper showed an unusually high result by x-ray fluorescence. No attempt was made to account for this discrepancy.

The analytical values by atomic absorption spectrometry are also shown in the table for comparison, since the results by this method are considered to be the most accurate. Fairly good agreement is seen between neutron activation analysis and atomic absorption spectrometry data.

Summary

A method to prepare a homogeneous dust sample of atmospheric particulate matter AS-1 was proposed. Elemental determinations were performed by use of neutron activation analysis, atomic absorption spectrometry, and x-ray fluorescence. A statistical evaluation of elemental distribution, homogeneity, was made with the analytical results. Analytical results of AS-1 by these methods suggest the usefulness of this sample.

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INDUSTRY TRENDS

Copeland Systems Inc. (Oak Brook, Ill.) has received a multi-million dollar contract from Nipro, Inc., for a Thermal Oxidation Reactor to destroy caprolactam plant organic effluents and produce clean liquid and gas, and by-product carbonate ash.

Resource Recovery Services, Inc., has been organized at Woodbridge, N.J., to provide consultation services regarding resource recovery from municipal and industrial solid waste.

Hoechst-Uhde Corp. (Englewood Cliffs, N.J.) received an EPA contract to develop a feasibility study for conversion of chlorinated hydrocarbon wastes to carbon tetrachloride. The technological basis is the Hoechst AG process from West Germany.

Republic Steel Corp. (Canton, Ohio) has announced the startup of a new stainless steel refining unit with a \$10 million air pollution control system using "one of the largest and most modern baghouses in the nation."

FMC Corp. has centralized its process development activities at Princeton, N.J. Among these activities is waste treatment improvement.

Anheuser-Busch Inc. (St. Louis, Mo.) announced that 23 of its Georgia distributors jointly contributed \$3000 to the National Center for Resource Recovery, Inc. (Washington, D.C.). Anheuser-Busch will match this contribution.

Shea Management, Inc. (Pittsburgh, Pa.) will provide association management services to the newly formed Recycling Equipment Manufacturers & Suppliers Association (REMSA).

Ferro-Tech, Inc. has designed, installed, and started up an automatic acid mine water neutralization system (750 000 gpd) in northern West Virginia.

The Carborundum Co. (Niagara Falls, N.Y.) announced that it will remain an active participant in the market for air pollution control.

Stanley Consultants, Inc. will make feasibility studies and develop engineering specifications for areawide waste treatment for the Kansas City area, under section 208 of P.L. 92-500.

NKK and Nihon Cement Co., both of Japan, have undertaken a joint study aimed at use of steel mill slag for cement production and as an aggregate for raw concrete.

Environmental Research & Technology, Inc., of Concord, Mass., has acquired Environmental Data Services, Ltd. (Denver, Colo.), and established a Rocky Mountain Technical Center in Denver.

Mitsubishi Petrochemical Co., Ltd. (Tokyo, Japan) will supply a commercial-scale electrolysis system for contaminated water purification at a \$570 million fertilizer plant Mitsubishi is building in Iraq.

Andco Inc. has formed the Andco-Torrax Division to market the firm's slagging pyrolysis-based solid waste conversion system in the U.S.

Ecodyne Corp.'s Cooling Products Division will install two concrete mechanical-draft cooling towers for Northern Indiana Public Service Co., at Wheatfield, Ind., for more than \$2 million.

The **Standard Oil Co.** (Ohio) has completed construction of an \$18 million air and water pollution control system at its refineries in Oregon.

Bell & Lupton Engineering Associates, Inc., has been formed at Chattanooga, Tenn. Pollution control will be among the services it provides.

A **Du Pont** "Permasep"-based reverse osmosis system will make water at Minotnas, Man., Canada, fit to drink by reducing dissolved solids from 3500 ppm to about 100 ppm.

Belco Pollution Control Corp. (Livingston, N.J.) has acquired the assets of Gerhard Hahn Associates, Inc. (Westwood, N.J.). Hahn is a firm of consulting structural engineers whose work includes flue systems for air pollution control equipment.

Ethyl Intertech Corp. is offering users of process, monitoring, and control equipment a reduced-rate periodic maintenance plan, which will generally be at \$26/h, including travel time.

Camp Dresser & McKee Inc. announced that a \$46 million advanced wastewater treatment plant is designed for the Metropolitan Sanitary District of Greater Chicago (Ill.) has started full-scale operations.

Velsicol Chemical Corp. (Chicago, Ill.) warns that society will pay \$1-3 billion/yr as a result of suspension of use of chlordane and heptachlor by the EPA. One example named was the costs generated by corn cutworms that will no longer be effectively controlled.

Swemco, Inc. (New York, N.Y.) has sold a venturi scrubber to Archer Daniels Midland (Decatur, Ill.) to clean exhaust gases from a carbon regenerator furnace, and abate dust. The carbon is used for sugar purification.

The SNC Group (Montreal, Canada) announced that an environmentally clean electrolytic zinc plant of its design is on stream for National Zinc Co., at Bartlesville, Okla. The plant uses the Belgian Vieille Montagne process.

Jacobs Engineering Co. (Pasadena, Calif.) is designing, engineering, and constructing a \$5 million dimer/polyamide plant at Dover, Ohio, for the Union Camp Corp.

Environmental Elements Corp. (Baltimore, Md.) has received an order from Caterpillar Tractor Co. (Mapleton, Ill.) for four automatic backwash and filters for industrial waste processing. Cost is about \$450 000.

Wedding/Allott & Lomax (St. Petersburg, Fla.), a professional association of C. Randolph Wedding AIA and Allott & Lomax (England), has been formed to service the U.S., the Caribbean, Central America, and Mexico. Part of the English firm's experience is in pollution control.

Uniroyal, Inc. (Detroit, Mich.) has begun marketing a new heavy truck radial tire that can help trucks meet forthcoming EPA noise standards.

The American Water Works Association has urged a year-long monitoring program for water-borne organics for the 420 largest surface-water supply sources. Estimated cost is \$4 million, or 5¢/person using this water.

The B.F. Goodrich Co. Chemical Division said that blood tests of its employees at the Port Neches, Tex., synthetic rubber plant, making styrene-butadiene rubber, showed no leukemia.

EN-CAS Analytical Laboratories has been reorganized as an independent company for environmental testing at Winston-Salem, N.C. Formerly, EN-CAS was a part of Ciba-Geigy (ES&T, April 1975, p 302).

Oil Mop, Inc. (New Orleans, La.) and **Marine Safety Services, Ltd.** (England) will assist the Spanish government in cleaning up a major oil spill at La Coruña, Spain, where more than 140 000 bbl were spilled.

NEW PRODUCTS

Energy resource recovery unit

The conically tapered, rotational hearth permits continuously controlled movement of waste and waste by-products. Ash transfer is automatic. The non-combustibles are recovered and the heat generated in the system can be converted into usable energy. Progressive Equipment Co. 101

Chemical, oil absorbent

The non-caking powder absorbs up to 200 times its weight in chemical and oil spills. It is non-flammable, contains no phosphates and will not irritate skin. Manostat Corp. 102

Organic water pollutant analyzer

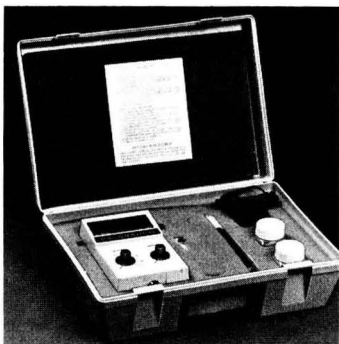
The system can capture and measure organic volatiles in the ppb range in potable water, plant effluents, or sewage. It will also measure total organic carbon. The system consists of a gas chromatograph, a sparger, reactors for TOC, stop-flow device and a pyrolysis probe. Chemical Data Systems 103

Tire shredder

The machine will shred six passenger or light-truck tires per minute; carbide tire studs and wire beads, belts and body plies are cut by its shearing action. No lubrication is needed. National-Standard Co. 104

Heat/line hose

Designed for use with equipment to monitor air and water pollutants, the high-temperature model provides heat up to 400 °F while the medium-temperature supplies heat up to 250 °F. The hose is available in sizes from 0.25–1.0 in. diameters and in lengths up to 100 ft. Its unitized construction offers greater flexibility. Technical Heaters Inc. 105

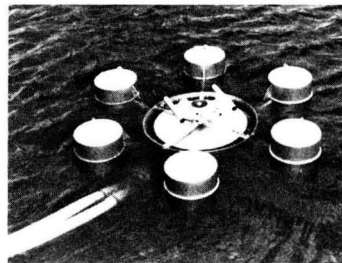


pH meter

The portable, digital meter is suitable for field and laboratory measurements. Its range is 0–14 pH units; its resolution 0.05 pH units, and its accuracy 0.03 pH units when standardized within 3 pH units. Balsbaugh Laboratories, Inc. 106

Portable cartridge recorder

The continuous loop, cartridge recorder with 0.25 in. eight-track tape is enclosed in a weatherproof suitcase. It is designed to accept a variety of support electronics for data acquisition in the field. L'Garde Products 107



Surface skimmer

Removes oil and other floating liquid or semi-liquid material from the surface of water. Features include a 3 in. outlet, a 27 in. weir, and six ballasts. Capacity governed by size of the pump, house, and material being skimmed. Industrial & Municipal Engineering Co. 108

Underwater measurement system

The portable transmissometer system can be used for turbidity, productivity and sedimentary studies. A recorder output allows on-site recording of the measurements. Martek Instruments, Inc. 109

Ball valves

The lockable swing-out valves find application in process lines, corrosive fluid systems and gas systems. The valves can be padlocked in the open or closed position. Pressure ratings are 2500 psi for stainless steel and 1500 psi for brass valves. Whitey Co. 110

Level monitor

The hollow stainless steel sensing probe can monitor process materials that are explosive, flammable or caustic. The electronics can be mounted up to 7 ft from the sensor. WESMAR 111

Carbon adsorption system

This non-regenerative system finds application in air exhaust from pulp and paper plants, sewage treatment plants and wherever toxic gases are emitted. Systems up to 5000 cfm are available. VIC Manufacturing Co. 112

Wave and tide gauge

Can sense rapid or gradual level changes in lakes, rivers, estuaries, coastal zones and open-ocean environments. Both remote and self-contained units are available. The unit's response time is adjustable, and a programmable timer permits selection of recording duration and periodicity. Bass Engineering, Inc. 113

Joint sealant

The Teflon fluorocarbon resin containing sealant hardens to an insoluble seal within 24 h. The sealant can be used in piping systems that convey chemicals, solvents, gases, and most industrial acids. Broadview Chemical Corp. 114

Oxygen analyzer

Instrument measures and indicates the oxygen level on a 0–5% scale or a 0–25% scale. The dial reading can be related to ppm of dissolved oxygen by using a nomograph. The instrument can aid in the maintenance of an oxygen level sufficient for bacterial decomposition of sewage. Edmont-Wilson 115

Flame photometric detector

This option added to the portable gas chromatograph permits the measurement of SO₂, H₂S, COS, and the mercaptans without interference the manufacturer claims. Phosphorus-base materials may also be measured with this detector. Analytical Instrument Development, Inc. 116

Sludge dewatering van

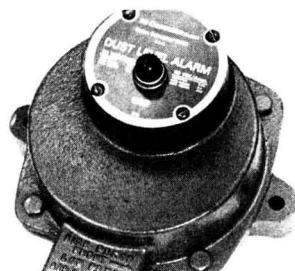
The mobile unit contains equipment for on-site testing to gather data to determine the best centrifuge for dewatering or the feasibility of vacuum filtration for dewatering. Envirex/Rexnord Co. 117

Boom

Designed to contain oil spills or to serve as oil slick barriers, the boom is manufactured in 20-ft sections with 9-in. diameters, polyfoam pellet-filled bladder and an 18-in. skirt and chain ballast. Sections can be connected by vinyl zippers. Environetics, Inc. 118

Data display system

System is designed to digitally display any selected 10 of 128 analog inputs in any range in three seconds. Input may be temperature, pressure, level or flow. Suntech Inc. 119



Dust level monitor

The unit senses when a predetermined level of fine, dry material is reached in a collection hopper and actuates an audible and/or visual signal. UOP Inc. 120

Hi-Vol timer

Designed for outdoor operations, the timer can control three 117 Vac, 25 amp circuits with an accuracy of ± 6 s/day. Environmental Measurements, Inc. **123**

Temperature indicator

The portable digital indicator displays temperature in degrees F or C. Operating range is 0–500 °C. The instrument has a standard linearized recorder output of 0.5 V/100 °C. C. W. Brabender Instruments, Inc. **124**

Telemetry system

Automatically monitors up to 10 operating and alarm conditions for single or multiple unit sewage lift stations, treatment plants and tertiary filter facilities. Can-Tex Industries. **125**

Environmental chamber

The cabinet can simulate altitude, temperature and humidity conditions. Cabinet capacities are available in 10, 15, 27, 36, 48, and 64 ft³. Altitudes up to 200 000 ft, temperatures from –100 to 350 °F, and relative humidity of 20–98% are offered. Tenney Engineering, Inc. **126**

Hi-Vol sampler

The unit samples ambient particulate matter. Standard features include a factory calibrated flow meter, a flow selector and a clear roof for easy filter inspection. Glass Innovations, Inc. **127**

Permeation device

Generates permeation rates of 500 000–1.5 million ng/min. These devices are intended for use in the calibration of stack air pollution monitoring systems. Average continuous life of the device is 1 yr; it is said to be stable for gases such as SO₂, H₂S and mercaptans. Ecology Board Inc. **128**



Gas monitors

Five monitors for O₂, CO, H₂S, NO₂, and SO₂ can be used for stack and ambient monitoring. Response time is 90% in about 3 min and accuracy is $\pm 2\%$. The units are battery operated and are suitable for environment spot checking. Joy Manufacturing Co. **129**

Sludge level controller

This ultrasonic system is suitable for use in thick opaque slurries and in slimy sludges such as raw sewage or industrial processing wastes. An integral relay with set point activates a sludge pump, valves and alarms. The output is standard for a chart recorder or remote readout. Markland Specialty Engineering Ltd. **121**

Noise level meter

Measures peak impact noise levels and displays these levels on a hold-type readout, and simultaneously measures continuous noise levels and displays these measurements on a second readout. Peak noise level measurements to 146 dB in a fast response hold, IEC impulse or OSHA impact mode are possible. Quest Electronics **122**

RO system

The reverse osmosis system can produce 25–500 gal/day of reagent-grade water. The unit operates at tap water line pressure or with a booster pump. Hydro Service & Supplies, Inc. **132**

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.

FIELD-PROVEN TOC-TOD ANALYZERS??

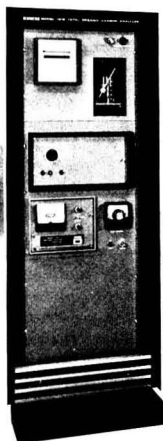
Talk to the people who have more of them in the field than anyone else.

If you're evaluating TOC-TOD analysis equipment, make sure you talk to the people who pioneered the technology... Ionics. With nearly 10 years in the field, Ionics has installed hundreds of units throughout the world that operate successfully on-line, day in and day out.

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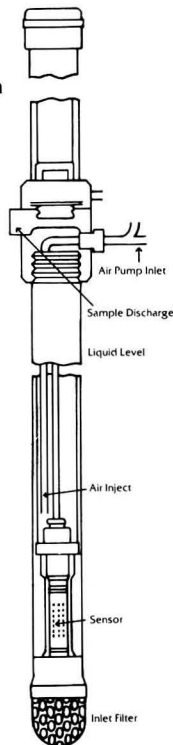


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Dissolved oxygen system that outperforms all others in activated sludge applications.

The Model 9407 DO electrode system features automatic self-cleaning and calibration checking functions. The Mackereth DO probe has large surface areas that are continuously scoured by the pumped sample.

Developed by EIL in England and exclusively distributed by Ionics, Inc. in the U.S.A.



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NEW LITERATURE

- Stack monitoring.** Suggested ordering specifications for requirements in stack emission monitoring systems are now available, and are based on EPA regulations as set forth in the *Federal Register*. Lear Siegler Inc. **151**
- Corrosion-resistant heating.** Price catalog lists a variety of heat exchangers, closed-loop, applicable to corrosion-resistant heating and cooling. Vulcanium Corp. **152**
- Scientific equipment.** "SCIENCE SPECIALTIES" catalog lists pH meters, calculators, pre-measured reagent standards, and other lines of scientific and laboratory equipment. Cole-Palmer Instrument Co. **153**
- Energy recovery services.** Brochure, "ERG/Energy Recovery Group", lists services designed to help businesses achieve better thermal utilization and economical air pollution regulation compliance. Dearborn Chemical (U.S.) **154**
- Ocean surveying.** Literature describes CESP II that can provide ocean bottom and sub-bottom data under poor acoustic conditions, high ship speed, and heavy weather, which normally cancels such activity. Raytheon **155**
- Water monitoring services.** Bulletin A-11000 describes high technology used to detect microcontaminants in water, as well as a portable virus monitor. The Carborandum Co. **156**
- Mass spectrometers.** Used equipment bulletin lists pre-owned mass spectrometers, leak detectors, and other analytical equipment for sale or lease. Scientific Products, Inc. **157**
- Gas chromatograph.** Bulletin 0107 describes the Series-R automated gas chromatograph with automatic gas sampling and backflush. Analysis times are shortened materially. Carle Instruments, Inc. **158**
- Wastewater centrifugation.** Bulletin 1225 describes advantages of centrifuges over other methods of thickening, classifying, and dewatering sludges. Sharples-Stokes Division, Pennwalt Corp. **159**
- Oxygen wastewater treatment.** Bulletin 8000-A reveals design characteristics of open-tank pure oxygen system for wastewater treatment with 90% or greater oxygen transfer. FMC Corp., Environmental Equipment Division **160**
- Pollution monitoring.** Flyer sheet tells how isotope-labelled compounds are useful for pollution monitoring, and lists company's line of these compounds. Prochem **161**
- Oil/water separation.** Brochure describes CATA-SEP oil/water separators, as well as wastewater treatment equipment and bacterial enzymes for treating effluents and controlling odors. MAPCO Inc. **162**
- Regulation compliance.** Bulletin ESP-8 lists programs that are designed to help companies comply with environmental regulations. Technical and economic feasibility studies are included. The Mogul Corp. **163**
- Meteorological instruments.** Catalog, "Complete Program of Lufft Recording Instruments", lists atmospheric temperature, pressure, and humidity recording instruments. Watrous & Co., Inc. **164**
- Vertical pumps.** Bulletin 60B1 tells about the Series 6000 vertical fiberglass pumps for heavy-duty applications, including suspended solids or corrosive fluids. Fyroc, Inc. **165**
- Resource recovery.** Brochure describes solid waste systems with emphasis on materials and energy recovery, and refuse-derived fuel. Refuse-derived fuel pellets are also covered. Grumman Eco-systems Corp. **166**
- Gas conditioners.** Brochure describes gas conditioners that filter out impurities from gas samples, so that samples can be used in EPA-approved source analyzers, such as those for SO_x and NO_x. Thermo Electron Corp. **167**
- Chemicals and safety.** 1976 Chemical Reference Manual lists line of chemicals, reagents, indicators, and other such materials, and discusses safe handling/storage/disposal of hazardous and toxic materials. MC/B Manufacturing Chemists **168**
- Centrifugal pumps.** Bulletin P-21-100a lists a complete line of centrifugal pumps, including Teflon pumps, self-priming pumps, and others. Capacities to 4800 gpm and heads to 720 ft. The Duriron Co., Inc. **169**
- Aerosol monitor.** Bulletin describes a portable means of determining the airborne mass concentration of respirable aerosols. One application is for OSHA testing. Measurement range 0.01-10 mg/m³ to particles less than 3.4 μ in size. THERMO-SYSTEMS Inc. **170**
- Radiodecontamination.** Brochure tells how company's product can be used for radioactivity decontamination. Atomic Products Corp. **171**
- Dust control.** Sheet describes European companies that manufacture industrial dust control equipment and other pollution control devices. DGE Vokes **172**
- Waste burning.** Brochure describes Thermal Reductor that burns solid, liquid, and gaseous wastes, meets particulate emission standards, and gives cost and maintenance savings. Progressive Equipment Co. **173**
- Bactericide.** Hiotrol Sanitizer brochure describes bactericidal/fungicidal properties of the Hiotrol Sanitizer, which uses an EPA-registered biocide. Technical data are given. Ferro Corp. **174**
- Laboratory equipment.** Catalog describes entire line of laboratory equipment for bio-medical, chemical, air, water, school, and other laboratories. Wheaton Scientific **175**
- Noise monitor.** Folder gives complete details on Model 614 portable noise monitor with a digital printout feature. Complete specifications are given. Bolt Beranek and Newman Inc. **176**
- Polymer pyrolysis.** "A Bibliography on the Pyrolysis of Vinyl and Condensation Polymers" gives wide coverage to this subject and to pyrolysis off-gas sampling and analysis. Wilks Scientific Corp. **177**
- Burner management.** Burner Management Systems brochure describes advanced burner management systems for control and more efficient burning in large utility and industrial boilers. Peabody Engineering Corp. **178**
- Clarifier.** Bulletin 128 describes peripheral feed clarifier for municipal and industrial wastewater applications. Engineering specifications are included. Lakeside Equipment **179**
- Air quality control.** Brochures describe air quality control with dry scrubbers and fluid-bed burners, as well as aluminum recovery and liquid waste treatment. Combustion Power Co. **180**
- OSHA limits.** Wall chart lists OSHA limits for gas and vapor concentrations, and accompanying brochure describes a portable ozone analyzer. Analytical Instrument Development, Inc. **181**
- Dust collector.** Bulletin 4500 describes new high-ratio Series 2000 fabric filter dust collector, and provides an application guide and engineering features. American Precision Industries Inc. **182**
- Better oil use.** "Fuel Oil Additives" describes how certain additives improve fuel

oil burning efficiency and reduce waste and equipment damage, as well as air pollution. Metropolitan Refining Co., Inc. **183**

Wet scrubber guide. Bulletin PC-10 discusses versatility of wet scrubbers in handling high temperatures and corrosive effluents which stem from metal processing. AMETEK, Inc. **184**

Laboratory equipment. "What's New for the Laboratory" No. 96 describes various kinds of analytical and other equipment, as well as a spill control center for hazardous chemicals. SGA Scientific **185**

"Teflon" filters. Brochure describes "Teflon" fluorocarbon fiber filters used in both wet and dry filtering applications. They enhance mist elimination and handle hot corrosive substances. Du Pont **186**

Sewage pumping. Bulletin 820-1 describes the Model "Six CC" self-contained sewage pumping station. Capacities are to 700 gpm with heads up to 200 ft. Enpo Cornell Pump Co. **187**

Reinforced plastic. Brochure tells about water/wastewater treatment capabilities of fiberglass-reinforced plastic, and about their use in fume systems, as well. Synerjenn Group **188**

Gas chlorination. Bulletins 3008, 3010, 3011, and 3013 list gas chlorination applications for water, freezing, hydraulics, and cooling water. Capital Controls Co. **189**

Dams. Three brochures describe the company's experience with the planning and design of dams. Harza Engineering Co. **190**

Laboratory supplies. Catalog lists laboratory supplies for biological, chemical, environmental, and nuclear applications. Safety supplies are also included. Interex Corp. **191**

Electrodialysis. Form No. 176-1214-76 explains electrodialysis (ED) and how it can be used for brine concentration, water treatment/reuse, and chemical processing. Dow Chemical U.S.A. **192**

Solid fuel burning. Brochure, "Field Draft Controls for Wood Burning Appliances", provides trouble-shooting information for burning this fuel, which is becoming a subject of resurgent interest. Conco Field Control Division **193**

Spectrophotometry. Illustrated brochure gives specifications and prices for a complete line of spectrophotometer cells and accessories for analysis. Ask for Catalog Q. Quaracell Products, Inc. **194**

Wet scrubbers. Bulletin No. 777 covers wet scrubber equipment and systems fabricated to meet the toughest federal, state, local, and industrial codes. The Willis & Paul Corp. **195**

Sample handling. Application note LSN 12 tells how samples handling and resolution are enhanced with fluorometric analysis by photon counting. Ortec Inc. **196**

Portable gas monitors. Folder PGM 50 includes information on six portable units that monitor NO_x, CO, oxygen, H₂S, NO₂ and SO₂. They apply to stack concentrations and OSHA requirements. Western Precipitation Division, Joy Manufacturing Co. **197**

Nondeterioration. "Studies on Nondeterioration of Air Quality" discusses possible effects of the Clean Air Act Amendments. It is an annotated bibliography. Robert T. Miki, Director, Office of Regulatory Economics and Policy, U.S. Department of Commerce, Washington, DC 20230 (write direct).

Waterworks. Brochure, "Water: Man's Greatest Single Need", tells of the company's services in the area of waterworks. George K. Tozer, Director of Water Division, Metcalf & Eddy Inc., 50 Staniford St., Boston, MA 02114 (write direct).

Automotive pollution. Booklet, "Automobiles and Air Pollution", suggests measures to be taken. Air Resources Board, 1709 11th St., Sacramento, CA 95814 (write direct).

OCS energy resources. Booklet explains leasing and management on the Outer Continental Shelf (OCS). Office of Communications, Department of the Interior, Washington, DC 20240 (write direct).

Coastal Zone. "Coastal Zone Management and Planning Publications". A list with descriptions. USC Sea Grant Institutional Program, University of Southern California, Los Angeles, CA 90007 (write direct).

Resource recovery. "Scrap Processors and Resource Recovery . . . The Need for Expanded Markets". Article. Institute of Scrap Iron and Steel, Inc., 1729 H St., N.W., Washington, DC 20006 (write direct).

Occupational health standards. Fluorides, phosgene, and kepone are covered. Publications-NIOSH, 4676 Columbia Parkway, Cincinnati, OH 45226 (write direct).

Environmental publication lists. Lists of publications and periodicals. Documentation & Library Services, National Environmental Engineering Research Institute, Nagpur-440 020, India (write direct).

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BOOKS

Economics of Transfrontier Pollution. 218 pages. OECD Publications Center, Suite 1207, 1750 Pennsylvania Ave., N.W., Washington, DC 20006. 1976. \$10.

The export of pollution is usually highly resented by the people of the receiving nation, and this report, containing eight technical papers, describes ways in which economic analysis can help to solve the transfrontier pollution problem. The economic instruments and various institutions available for this effort are exhaustively analyzed and described.

Ambient Air Quality Standards—Here We Are, What Do We Do? William J. Moroz and George C. Wiedersum, Eds. 264 pages. The American Society of Mechanical Engineers, Order Dept., 345 E. 47th St., New York, NY 10017. 1976. \$30, paper.

Should reliance on domestic fuels be increased, even at the risk of not meeting ambient air quality standards? Were measures taken to comply with these standards contributory factors for increased dependence upon foreign sources of fuel? This book contains proceedings of an ASME symposium in which there was discussed how this dilemma could be resolved, and covers air quality standards, compliance schedule effects, new control technology, and other pertinent topics. Ask for Book No. 100099.

Resource Recovery and Conservation. James G. Abert and Harvey Alter, Eds. Periodical. Elsevier Scientific Publishing Co., P.O. Box 211, Amsterdam, The Netherlands. Volume 2, 1976. \$41.95/year.

In this quarterly periodical, many aspects of solid waste are discussed. These include energy recovery, economics of materials recovery, markets, single-cell protein culture, municipal disposal, bioconversion, and many other topics. The editors are with the National Center for Resource Recovery (Washington, D.C.).

Energy Law & Regulations. 144 pages. Government Institutes, Inc., 4733 Bethesda Ave., Bethesda, MD 20014. 1976. \$25.

Last December 22, the new energy law, P.L. 94-163, was enacted, and an Energy Law Seminar was convened in January to evaluate the impact of this law on industrial energy users. Among subjects discussed are natural gas, the Federal Power Commission, environmental considerations, coal and electricity, and federal assistance for energy shortages. While environmental considerations stress air, other aspects are covered.

Clinical Implications of Air Pollution Research. Asher J. Finkel and Ward C. Duel, Eds. 374 pages. Publishing Sciences Group, Inc., 162 Great Road, Acton, MA 01720. 1976. \$20, casebound.

The object of this book is to provide a greater understanding of the relationship between air pollution exposure and human illness. Symptoms and documented evidence are presented, and the amount of pollution that can be borne, with effects at different contamination levels, is evaluated. Fifty concerned specialists contributed to this book which grew out of the American Medical Association Air Pollution Research Conference, held at San Francisco, Calif.

Thermal Processing of Municipal Solid Waste for Resource and Energy Recovery. Norman J. Weinstein and Richard F. Toro. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, MI 48106. 1976. \$20.

This work is a critical analysis of thermal processing of solid waste for energy recovery and resource recycling. Pyrolysis processes, thermal processing, costs, and resource and energy recovery are discussed in depth. Also included are chapters on air pollution control and liquid and solid residue disposal.

Occupational Carcinogenesis. Umberto Saffiotti and Joseph K. Wagoner, Eds. 516 pages. The New York Academy of Sciences, 2 E. 63rd St., New York, NY 10021. 1976. \$39 (add \$1 for mailing), paper. Ask for Annals, Volume 271.

Since 1775, there have been connections known between occupations and increased cancer rates. This volume traces that history, discusses such relationships and connections found from that year to this decade, and discusses this "time bomb" occupational hazard from many aspects, and in great detail. Numerous industries are covered in this collection of papers presented at a conference on this subject held by the Academy in March 1975.

Thermal Processing of Municipal Solid Waste for Resource and Energy Recovery. Norman J. Weinstein and Richard F. Toro. xix + 179 pages. Ann Arbor Science Publishers Inc., P.O. Box 1425, Ann Arbor, MI 48106. 1976. \$20, hard cover.

Combustion and pyrolysis of solid wastes is coming under increasing scrutiny as a possible energy source; indeed, these methods are operational in some places. This book discusses theory, practicality, and costs of such systems, as well as markets for recovered energy and

resources. Systems sufficiently advanced and attractive to be considered for projects in the near future are also covered, as are pollution control considerations.

Survival: It's Up To Us. Luis A. Torres. 159 pages. Vantage Press, Inc., 516 W. 34th St., New York, NY 10001. 1976. \$4.95, hard cover.

The author suggests what he believes to be a simple, inexpensive way to clean up polluted streams, rivers, and lakes. To back up his ideas, he presents capital and operating cost estimates, and projected income figures. He calls for cooperation with the laws of nature, rather than attempts to change them; attempts, he believes, are ultimately bound to fail.

Environmental Indices. Herbert Inhaber. xiv + 178 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1976. \$14.50, hard cover.

Is the environment getting better or worse? An index, much as is used to assess the economy, is needed for an environmental assessment, and this book provides such an index. To make things clear, "environment" is broken down into air, water, land and the like, and into subcategories where necessary. Each is evaluated, and ways in which an intelligent evaluation of the environment can be made are presented clearly and simply.

Air and Water Purification and Pollution Control Equipment. v + 215 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. 1976. \$3.40, paper.

This report is a Global Market Survey of the Department of Commerce (DOC) which covers 20-30 of the best foreign markets for an industry or group of related industries. It describes major foreign markets for this industry, breaks them down by country, and describes U.S. government services available to exporters. Promotional events are also listed.

The Environmental Control Industry. Kenneth Ch'uan-k'ai Leung and Jefferey A. Klein. 138 pages. Ann Arbor Science Publishers Inc., P.O. Box 1425, Ann Arbor, MI 48106. 1976. \$14.95, paper.

This report analyzes many aspects and factors of this industry. It discusses the types of firms one finds in the field, and takes an exhaustive look at markets for equipment in air and water pollution, and solid waste. The authors, financial analysts, prepared the report for the Council on Environmental Quality.

Build Your Own Solar Water Heater. 25 pages. Environmental Conservation Center of the Florida Conservation Foundation, Inc., 935 Orange Ave., Winter Park, FL 32789. 1976. \$2.50, paper.

Here is a way to have hot water, and a reduction in fuel prices. Included in this booklet is a step-by-step set of instructions that should, if properly followed, provide an effective solar hot water heater.

Methodologies for the Determination of Stream Resource Flow Requirements. J. L. Arnette and C. B. Stalnaker, Eds. 199 pages. National Technical Information Service, Springfield, VA 22161. 1976. \$7.75, paper; \$2.75, microfiche. Ask for PB 253152.

What are effects on fish and terrestrial wildlife when stream flow through their habitats is changed, and how can these effects be measured? Can there be alterations without significantly changing conditions for fish and wildlife, as well as environmental values? This report takes a major step toward answering these questions, and tells how such changes might be anticipated. It was prepared at Utah State University for the U.S. Fish and Wildlife Service.

Air Pollution Chart. Roy G. Scarfo, Inc., P.O. Box 217, Thorndale, PA 19372. 1976. \$2.75.

This 28 X 23 in. chart provides a pictorial survey of air pollution in the U.S. It includes various facts and charts about the atmosphere, and provides a nationwide picture of concentrations, sources, and volumes of emissions of major pollutants. Effects on plants and the human body are also shown.

The Claus Process. 50 pages. R. H. Chandler Ltd., P.O. Box 55, Braintree, Essex CM7 6HD, England. 1976. \$15, paper.

Many government regulations now require, or will call for reduction of sulfur emissions to the atmosphere to very low levels. With new technology, more efficient stripping of sulfur from tail gases becomes possible. This bibliography reviews 66 literature references and provides abstracts of 95 patents in this technology from 9 countries.

Disposal in the Marine Environment: An Oceanographic Assessment. 76 pages. National Academy of Sciences, 2101 Constitution Ave., N.W., Washington, DC 20418. 1976. \$5.

In this report, the Academy recommends that a comprehensive understanding of nearshore oceanography be developed, as well as properties of wastes, and techniques for handling them. The report is meant to be a guide for waste management planners, and those who would influence them, to points of ocean science and their implications for coastal waste management.

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August 19–20 New York, N.Y.
Energy Conservation in Plants. 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

August 19–22 Princeton, N.J.
1976 Solar Trade Show. Allied Service Group

Write: Allied Service Group, 252 Nassau St., Princeton, N.J. 08540

August 29–September 3 San Francisco, Calif.
American Chemical Society's Centennial Meeting. American Chemical Society (ACS)

Environmental topics will be discussed. *Write:* A. T. Winstead, ACS, 1155 16th St., N.W., Washington, D.C. 20036

September 7–10 Biloxi, Miss.
U.S. Water Resources Council and Interstate Conference on Water Problems (WRC/ICWP) Meeting. U.S. Water Resources Council and Interstate Conference on Water Problems

Write: Jim Fish, assistant secretary treasurer of ICWP, c/o F. Robert Edman and Associates, W-3173 First National Bank Building, St. Paul, Minn. 55101

September 12–16 Las Vegas, Nev.
Annual Convention and Exposition. National Water Well Association (NWWA)

Write: Jay H. Lehr, NWWA, 500 W. Wilson Bridge Rd., Worthington, Ohio 43085

September 12–17 Oxford, Ohio
Emission Sampling for Source Evaluation. Engineering Foundation

Write: Engineering Foundation Conferences, 345 E. 47th St., New York, N.Y. 10017

September 12–17 Raleigh, N.C.
International Conference on Photochemical Oxidant Pollution and Its Control. U.S. EPA

Write: Mrs. Enestine McIver, administrative secretary, Triangle Universities Consortium on Air Pollution, P.O. Box 2284, Chapel Hill, N.C. 27514

September 12–17 State Line, Nev.
11th Intersociety Energy Conversion Engineering Conference. American Chemical Society, American Institute of Chemical Engineers and others

Write: Elton J. Cairns, General Motors Research Labs, 12 Mile & Mound Rds., Warren, Mich. 48090

September 13–15 Washington, D.C.
OCEANS 76. Marine Technology Society (MTS) and the Institute of Electrical and Electronics Engineers (IEEE) Council on Oceanic Engineering

Environmental topics will be discussed. *Write:* OCEANS 76 Conference Staff, 730 M St., N.W., Suite 412, Washington, D.C. 20036

September 13–17 Berkeley, Calif.
4th Annual Conference on Nuclear Power and Environmental Assessment. College of Engineering and Continuing Education in Engineering, University of California—Berkeley

Write: Continuing Education in Engineering, University of California Extension, 2223 Fulton St., Berkeley, Calif. 94720

September 13–17 Edgewood Arsenal, Md.

Seventh Annual Environmental Research Symposium. American Defense Preparedness Association (ADPA)

Topics include environmental technology, and military waste effluents. *Write:* Col. Robert D. Worthen, ADPA, 819 Union Trust Building, 740 15th St., N.W., Washington, D.C. 20005

September 14–16 Los Angeles, Calif.
Nuclear Power Plant Construction, Licensing and Startup. American Nuclear Society

Write: Frank D. Ducey, Pickard, Lowe and Garrick, Inc., 200 Newport Center Dr., Suite 312, Newport Beach, Calif. 92660

September 15–17 Anchorage, Alaska
1976 Annual Meeting. Pacific Northwest International Section/Air Pollution Control Association (PNWIS-APCA)

Theme is "The Effect of Alaska Resource Development on Western North America." *Write:* Fluor Alaska, Inc., 1577 C St., Anchorage, Alaska 99501

September 16–17 Chicago, Ill.
Fourth Annual Illinois Energy Conference on Illinois Coal. Energy Resources Center/University of Illinois at Chicago Circle and the Energy Research and Development Administration and others

Environmental issues will be considered. *Write:* Energy Resources Center, University of Illinois at Chicago Circle, Box 4348, Chicago, Ill. 60680

September 19–24 Merrimac, Wis.
Penrose Conference on the Hydrogeologic Regime of Inland Lakes. The Geological Society of America

Attendance will be limited to 70. *Write:* D. A. Stephenson, Environmental Resources Unit, 1815 University Ave., Madison, Wis.

September 19–24 Oxford, Ohio
Present Status and Research Needs in Energy Recovery from Wastes. The Engineering Foundation

Write: Engineering Foundation Conferences, 345 E. 47th St., New York, N.Y. 10017

September 20–21 Rochester, N.Y.
36th Congress on Occupational Health. American Medical Association and the National Institute for Occupational Safety and Health

Write: American Medical Association, Dept. of Environmental, Public and Occupational Health, 535 N. Dearborn St., Chicago, Ill. 60610

September 20–24 Gaithersburg, Md.
8th Materials Research Symposium: Methods and Standards for Environmental Measurement. U.S. Dept. of Commerce/National Bureau of Standards

Write: Office of Air and Water Measurement, National Bureau of Standards, Room A345, Chemistry Building, Washington, D.C. 20234

Courses

August 23–24 Madison, Wis.
Nuclear Fuel and Waste Management, Course No. 540. University of Wisconsin—Extension

Fee: \$110. *Write:* University of Wisconsin—Extension, 432 N. Lake St., Madison, Wis. 53706

August 23–27 Appleton, Wis.
Water and Waste Water Control. Institute of Paper Chemistry

Fee: \$500. *Write:* Dr. T. A. Howells, Director of Continuing Education, The Institute of Paper Chemistry, P.O. Box 1039, Appleton, Wis. 54911

August 24–26 Madison, Wis.
Water Quality and Land Use Mapping. University of Wisconsin—Extension, Dept. of Engineering

Fee: \$175. *Write:* John T. Quigley, program director, Dept. of Engineering, University of Wisconsin—Extension, 432 N. Lake St., Madison, Wis. 53706

September 1 New Brunswick, N.J.
Recertification for Visual Emissions Evaluation. Cook College/Rutgers the State University of New Jersey

Fee: \$85. *Write:* Dept. of Environmental Science, Cook College, Rutgers University, P.O. Box 231, New Brunswick, N.J. 08903

September 8–10 Washington, D.C.
Preparation of Environmental Impact Statements. The George Washington University

Fee: \$320. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

September 13–16 Los Angeles, Calif.
Control of Particulate Emissions, Course No. 413. Air Pollution Training Institute

Fee: \$88. *Write:* Registrar, Air Pollution Training Institute, MD-17, Environmental Research Center, Research Triangle Park, N.C. 27711

September 26–October 1 Easton, Md.
Land Application of Residual Materials. The Engineering Foundation and the American Society of Civil Engineers

Attendance is limited to 100. Fee: \$250. *Write:* The Engineering Foundation Conferences, 345 E. 47th St., New York, N.Y. 10017

(continued on page 830)

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Contact: Please send a detailed resume including salary history or a completed Standard Form 171 (Personal Qualifications Statement), which can be obtained from any Federal Government personnel office, to reach EPA no later than September 2, 1976, to Mrs. Edna Morse (PM-212), Personnel Management Division, Environmental Protection Agency, 401 M Street, S.W., Washington, D.C. 20460

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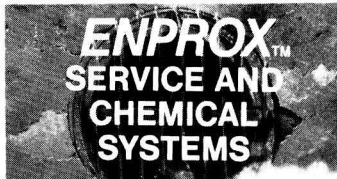
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 Fee: None. Write: Navy Environmental Health Center, 3333 Vine St., Cincinnati, Ohio 45220

International

September 22–24 Düsseldorf, Germany
International Colloquium on Ozone and Related Substances in Photochemical Smog. VDI-Kommission Reinhaltung der Luft
 Write: Secretariat, VDI-Kommission Reinhaltung der Luft, Postfach (P.O.B.) 1139, D-4000 Düsseldorf, Germany

September 24 Ottawa, Canada
Physics of the Environment. Carlestone University Dept. of Physics
 Write: Dr. Herbert Inhaber, Advanced Concepts Centre, Planning & Finance Service, Environment Canada, Ottawa, Canada K1A 0H3

September 27–October 1 Jonkoping, Sweden
Second AVFALL International Trade Fair on Waste Handling, Waste Recovery and Industrial Cleaning. AVFALL
 Write: Gerald G. Kallman, U.S. Representative for ELMIA, 30 Journal Square, Jersey City, N.J. 07306

October 17–22 Sydney, Australia
8th International Conference on Water Pollution Research. International Association on Water Pollution Research (IAWPR)
 Write: IAWPR, 8th International Conference, G.P.O. Box 2609, Sydney N.S.W. 2001, Australia

October 21–22 Antwerp, Belgium
First International Symposium: Materials and Energy from Refuse. European Federation of Chemical Engineering
 Write: Materials and Energy from Refuse, Jan van Rijswijcklaan 58, B-2000 Antwerp, Belgium

November 14–19 Caracas, Venezuela
International Symposium on Industrial Wastes and the Environment. International Association of Medicine and Biology of the Environment
 Write: Dr. Richard Abbou, 115, rue de la Pompe, 75116 Paris, France

December 6–10 Paris, France
International Congress of the Environment. Compagnie Francaise d'Editions (CFE), Département Congrès
 Write: Secrétariat général, Assises Internationales de l'Environnement CFE, 40 Rue du Colisée, 75008 Paris, France

December 7–11 Paris, France
2nd International Environmental Week: 1st International Exhibition of Air, Noise, Waste and Water Techniques and other exhibitions. Minister of the Quality of Life and the Minister of Labor
 Write: Jean-Loup Gallien, Technoexpo, 8, rue de la Michodière, 75002 Paris, France

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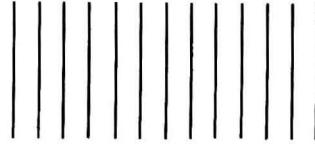
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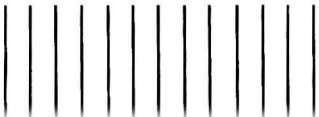
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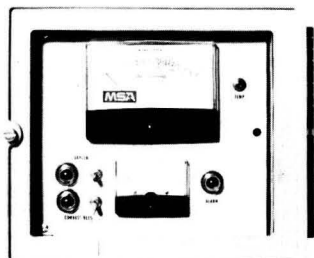
COMBUSTION CONTROL • HEALTH & SAFETY • ENVIRONMENTAL • PROCESS

New-generation oxygen analyzer for combustion control cuts emissions, pays itself off in months.

Unburned fuel going out your stack means pollution. But just as important, it means you are wasting expensive fuel. Accurate monitoring of excess air will permit you to save fuel and avoid the loss of Btu's up your stack.

MSA's new Model 803 Oxygen Analyzer was designed to solve many of the practical operating problems that you face in accurate monitoring of O_2 in hot, dirty flue gases.

The Model 803 sensor cell mounts directly on the stack for shortest possible sampling line. It operates hot to keep all gases above their dew points and minimize plugging. The stabilized fuel sensor measures oxygen—not an effect of oxygen—so it produces a high-level signal. It analyzes 0.1% to 21% O_2 . The lower the oxygen concentration, the better the readability on its logarithmic scale.



Users of the Model 803 Oxygen Analyzer have commented on its fast response to changes in furnace operating conditions. And its close matchup between oxygen readings and theoretical calculation of O_2 content gave them fuel savings that paid for the analyzer quickly.

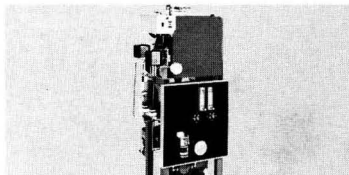
One chemical company made a comprehensive study of heat loss. They found that oxygen analysis with the zirconium oxide cell, the type used in the Model 803, overcame the operating problems and the need for frequent maintenance found in other types of sensors.

They also reported to their operating group that use of such an analyzer for excess air control could save about \$1,500 a month, if the efficiency of a 200,000-lb/hr boiler was increased by just 1%. This calculation was based on 26¢ fuel oil, 335 days of 24-hour operation per year.

If you need a dependable, accurate oxygen analyzer that stays out of trouble and saves you fuel, get details on the Model 803.

Circle No. 37

SO_2 , NO and CO analysis in stack gases made simpler, more accurate.



MSA now offers custom-designed Stack Analysis Systems which include a compact extractive sample acquisition and conditioning system. You have a choice of free-standing cabinets or wall-mounted housings, and provisions are available for single-point or multipoint sampling, or for one or more contaminants.

The analysis train starts with a specially designed 5-micron shielded-filter probe mounted directly in the stack. The heat-traced sampling line is maintained at a temperature high enough to keep the sample gas above the dew point, so that any water vapor remains in the vapor state. The sample is quenched quickly and dried after it enters the conditioning system, without any appreciable loss of SO_2 content. The entire sampling train is built of corrosion-resistant materials to minimize both maintenance and possible contamination.

The cooled gas sample then passes

through a series of filters which removes the balance of the particulate matter. Finally it enters the analyzer through a selector valve and flowmeter. Several different analyzers can be provided with a conditioned sample from this system, and the system is provided with a bypass flow to minimize sample transport time. MSA can provide high-reliability analyzers for continuous monitoring of SO_2 , NO, CO, CO_2 , total hydrocarbons and solvent vapors. The typical unit shown here uses a LIRA® Infrared Analyzer, calibrated for analysis of SO_2 in the 0-2000 ppm range. Zero and span gas test connections are provided for easy calibration check.

For heavy dust-loading applications—BOFs, cement kilns, cupolas, blast furnaces—MSA offers special heated filter systems. There are also pressure switches or gages to indicate plugged sample lines, and automatic back purge of traps, probes and sample lines is provided.

The MSA® Stack Analysis System can be interfaced with any recording, alarm or computer readout; and composition signals can be used with flow rates to calculate mass emissions in pounds per hour. Discuss your needs with an experienced MSA instrument specialist.

For details circle No. 38

Versatile infrared analyzers monitor everything from solvent vapors to carbon monoxide.

MSA introduced the LIRA Infrared Analyzer over 20 years ago, and we find new applications for it every year. One reason is the instrument's unique ability to select a specific component out of a mixture of gases (or liquids) and record its concentration quickly, accurately and dependably over a broad ambient temperature range. Another reason is the flexible design of the LIRA. We can offer a wide choice of cell lengths and materials, peripheral readout equipment and types of housings.

Among the LIRA systems we have supplied for pollution control are:

- A stack analysis system for 0-2000 ppm SO_2 .
- Air monitoring network of LIRA detectors for CO.
- An automobile-emissions screening installation where LIRA analyzers are combined with instruments and readout meters for CO, HC, and NO in exhaust gases.

Some typical health-and-safety and process applications in current use include:

- A 5-point CO_2 detection system to protect brewery workers.
- An 8-point system for 0-2000 ppm acetone in air.
- A 10-point system for 0-1000 ppm methylene chloride in air.
- Multipoint halocarbon gas detection and alarm system for 0-3000 ppm CHCl_3 .
- A 5-point system for 0-200 ppm of trichloroethylene (in combination with an MSA Model I-500 Combustible Gas Detector).
- Multipoint CO_2 detector for process control in the 15-35% range, on a lime kiln.
- CO_2 detection at 0-100 and 0-1500 ppm range to guard LNG liquefaction equipment from plugging.

These are just a few of the thousands of LIRA analyzers in every type of industry today. There has to be a reason. Check it out for your OSHA, stack monitoring, process control or air monitoring problems.

Circle No. 39

Ask us for details.

Get the latest literature on the MSA monitoring instruments described here. Circle the appropriate Reader Service Number. MSA Instrument Division, 400 Penn Center Boulevard, Pittsburgh, Pa. 15235.


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