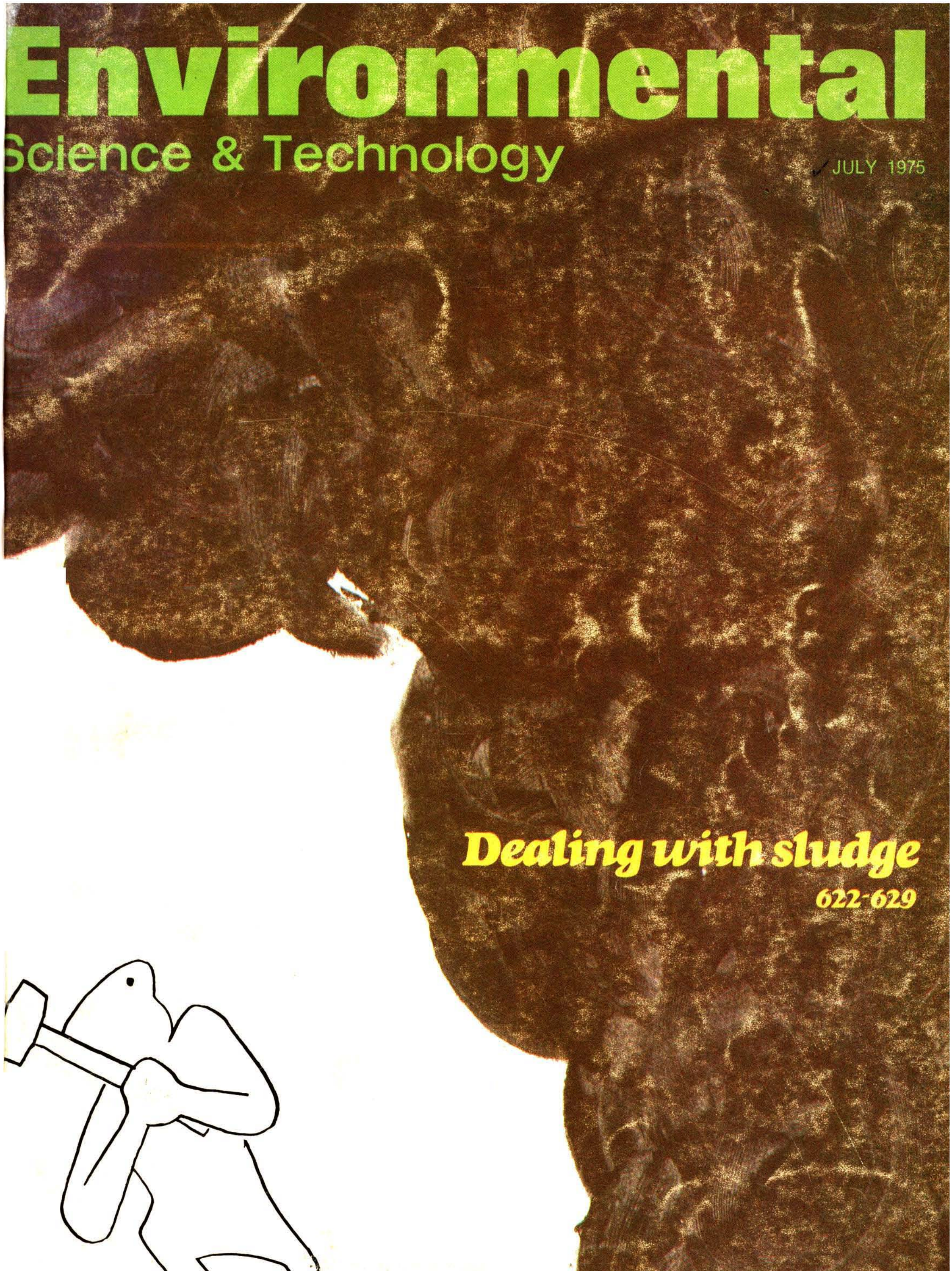
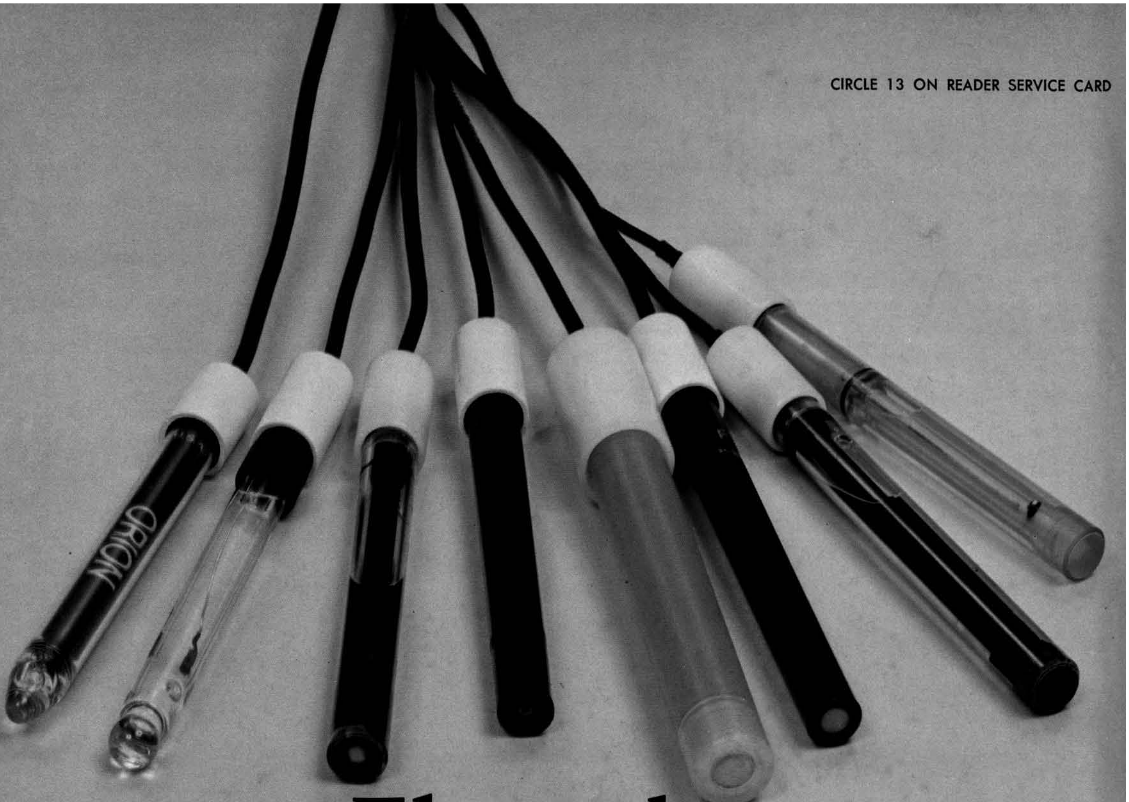
Environmental
Science & Technology

JULY 1975



Dealing with sludge
622-629

CIRCLE 13 ON READER SERVICE CARD



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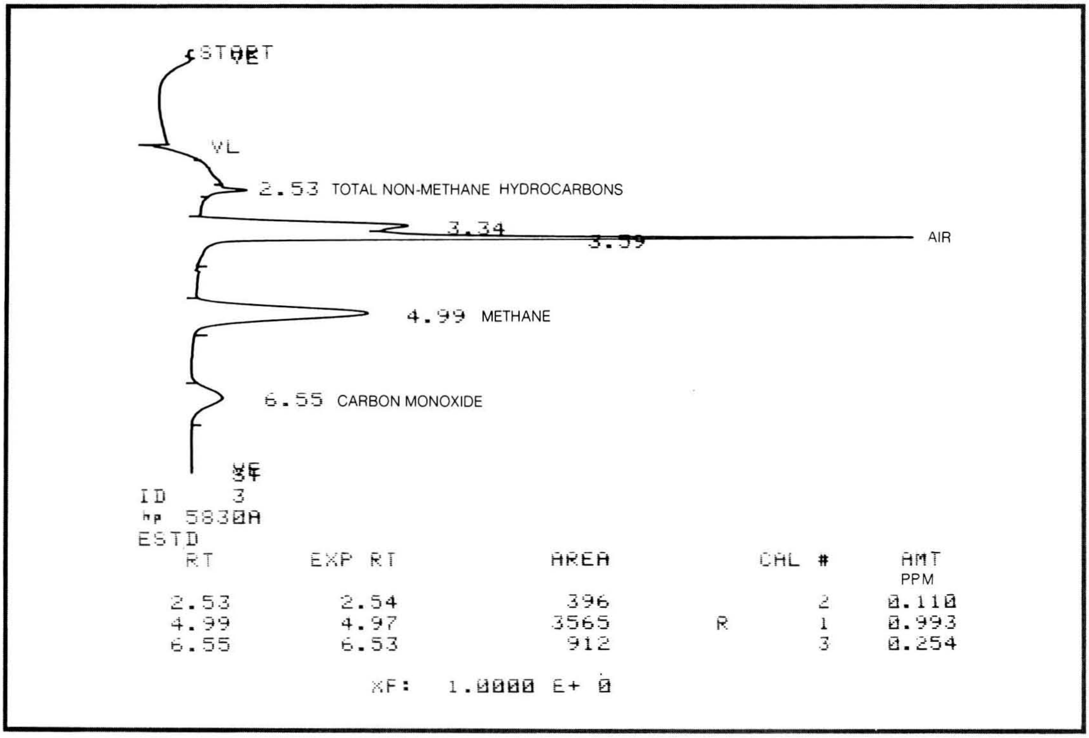
ORION RESEARCH



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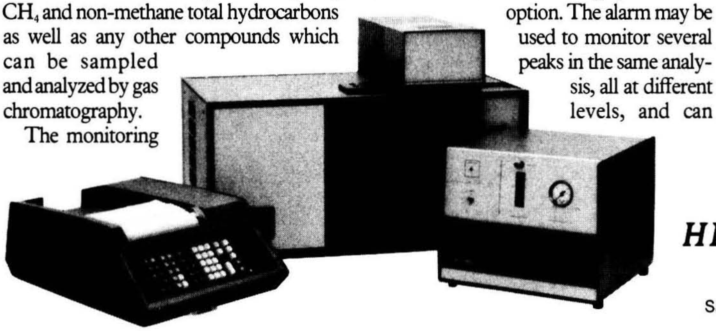

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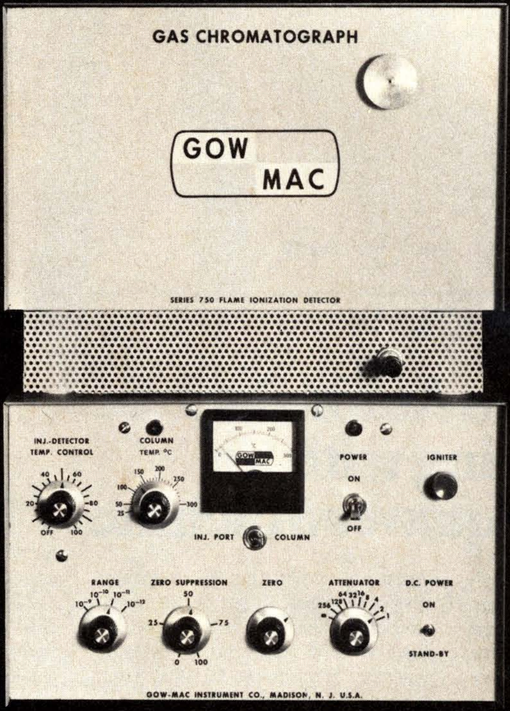

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CIRCLE 26 ON READER SERVICE CARD

Environmental Science & Technology

Volume 9, Number 7, July 1975

ESTHAG 9(7) 605–694 (1975)
ISSN 0013-936X

CONTENTS

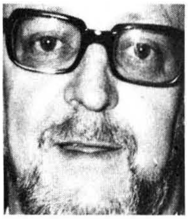
Features

PAT report

Outlook

Departments

Current research



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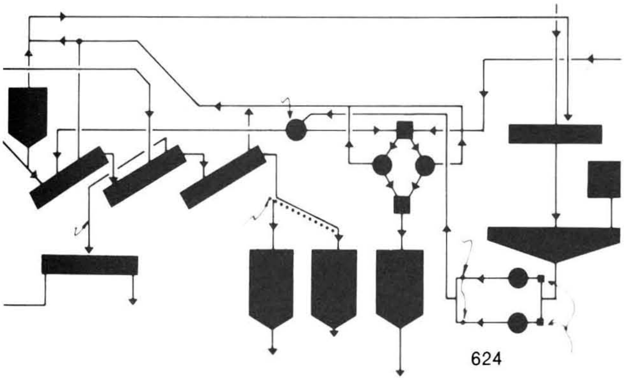

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Published monthly, with additional Pollution Control Directory in October, by the American Chemical Society, from 20th and Northampton Sts., Easton, Pa. 18042.•Executive offices: Editorial Headquarters, 1155 16th St., N.W., Washington, D.C. 20036. Advertising office: 50 West State St., Westport, Conn. 06880. Second-class postage paid at Washington, D.C., and at additional mailing offices.

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CURRENT RESEARCH

Problems of measuring and predicting influence of effluents on marine phytoplankton 635

W. M. Dunstan

Algae cultures failed to grow at predicted levels on the basis of increased nitrogen and phosphorus levels from added sewage effluent. The role of minor growth substances in controling phytoplankton product is stressed.

Trees as environmental sensors monitoring long-term heavy metal contamination of the Spokane River, Idaho 638

J. C. Sheppard* and W. H. Funk

Pine trees are used to monitor past concentrations of heavy metals by neutron activation of core sections and tree rings. Rough agreement is found with Coeur d'Alene Lake sediment core data and the ore mining volume if metal holdup by the lake is considered.

Concentration and size of trace metal emissions from a power plant, a steel plant, and a cotton gin 643

R. E. Lee, Jr.,* H. L. Crist, A. E. Riley, and K. E. MacLeod

A cascade impactor was used to determine the size distribution of particles from a power plant, a steel plant, and a cotton gin, before and after installation of emission control systems. Efficiency of the baghouse and electrostatic precipitators was at least 98% for submicrometer size particles.

Reactivities of complex hydrocarbon mixtures 648

S. L. Kopczynski, R. L. Kuntz, and J. J. Bufalini*

Hydrocarbon mixtures were irradiated in a large chamber. Rates of oxidation of NO, NO_2 dosage, hydrocarbon usage, eye irritation, and yields of PAN, formaldehyde, and oxidant were measured. Changes in parameters by substituting aromatics for olefins, or paraffins for aromatics are discussed.

Rapid formation of iminodiacetate from photochemical degradation of Fe(III)nitrilotriacetate solutions 654

R. J. Stolzberg and D. N. Hume*

Fe(III)nitrilotriacetate rapidly undergoes stoichiometric photodegradation when exposed in sunlight to iminodiacetate. This is very slowly degraded to glycine. Accumulation of iminodiacetate is of concern because of the possible carcinogenicity of *N*-nitroso iminodiacetic acid.

Characterization of Australian crudes and condensates by gas chromatographic analysis 656

B. W. Jackson, R. W. Judges, and J. L. Powell*

This technique uses only that portion of crude petroleum boiling between 232° and 316°C. From this fraction, a number of quantifiable parameters can be determined. A number of Australian crudes and condensates are characterized by this method.

Iodate formation and decomposition in iodometric analysis of ozone 660

D. L. Flamm* and S. A. Anderson

A second product in addition to iodine is formed during absorption of ozone with "neutral" buffered KI. This is concluded to be iodate. The formation and decomposition of this compound should be considered in ozone analysis.

Ambient air analysis with dichotomous sampler and X-ray fluorescence spectrometer 663

T. G. Dzubay* and R. K. Stevens

Air samples collected with a dichotomous sampler were analyzed by X-ray fluorescence. Seventy-five percent of the S, Zn, Br, and Pb was found in particles smaller than 2 μm, and 75% of the Si, Ca, Ti, and Fe occurred in particles larger than 2 μm.

Distribution of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in aquatic model ecosystem 668

A. R. Isensee* and G. E. Jones

Several organisms were exposed to ^{14}C-labeled TCDD in a model ecosystem for up to 31 days. Accumulation by all organisms was directly related to water concentration. No metabolites of TCDD were found.

NOTES

Operational characteristics of vibrating orifice aerosol generator 673

J. B. Wedding

A scaling parameter which eliminates the need to experimentally establish correct modulation frequencies is calculated. Monodisperse frequency range of the vibrating orifice aerosol generator can be found by optical sizing and selection of reasonable flow rates.

Facile incorporation of chlorine into aromatic systems during aqueous chlorination processes 674

R. M. Carlson,* R. E. Carlson, H. L. Kopperman, and Ronald Caple

Chlorine is easily incorporated into aromatic compounds under conditions normally used for water chlorination. The extent of incorporation varies with pH and contact time.

Oxidation of cinnabar by Fe(III) in acid mine waters 676

J. E. Burkstaller,* P. L. McCarty, and G. A. Parks

Fe(III) oxidized cinnabar in acid mine waters, releasing mercury into solution. Total mercury released was measured by an isotopic dilution technique. Most of the oxidized mercury remained bound to the cinnabar by some unknown mechanism.

Interference of sulfate ion on SPADNS colorimetric determination of fluoride in wastewaters 678

R. F. Devine* and G. L. Partington

Serious errors in the approved SPADNS method for fluoride analysis of wastewaters are caused by sulfate ion carry-over from the initial distillation step. The use of a fluoride ion electrode is suggested as a better method.

Credits: 615, C&EN's Janice Long; 619 (two photos), *ES&T*'s Julian Josephson; 620, Sharri Harris; 622, U.S. Dept. of Transportation; 625 (left), De Bruyn (Burlington, Ont.); 625 (right), The Riffle Co. (Warren, Ohio); 629 (upper), Moffett Studio (Chicago)

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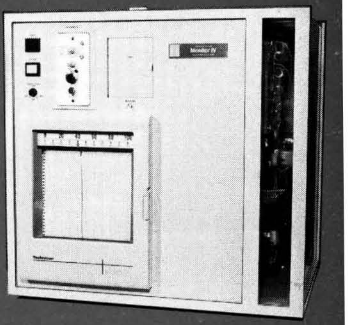
* To whom correspondence should be addressed.
This issue contains no papers for which there is supplementary material in microform.

Monitoring Security



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*Analytical Quality Control Newsletter, EPA, Cincinnati: Issue No. 21, April, 1974; page 13
† Federal Register, October 16, 1973

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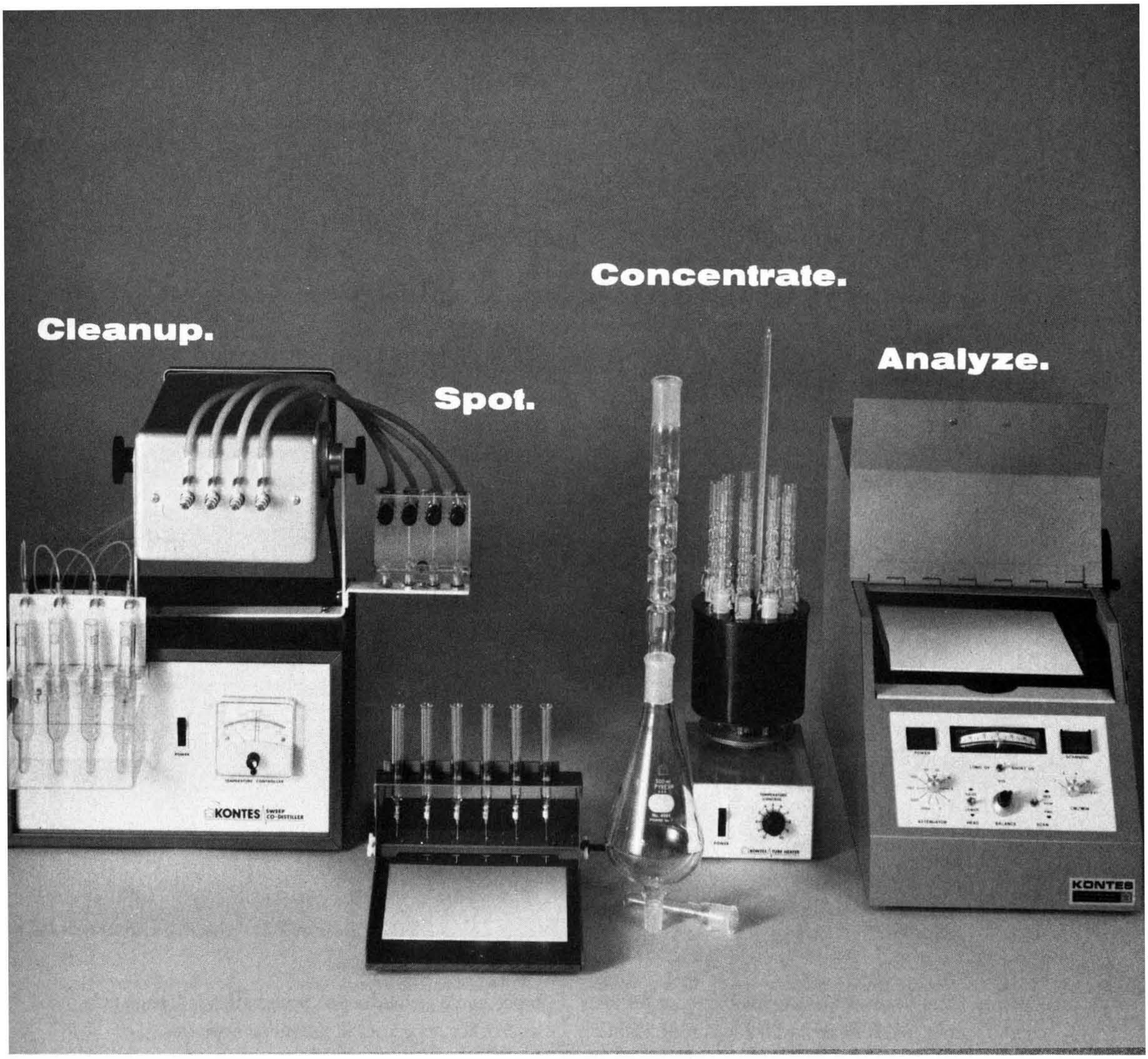
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LETTERS

More on monitoring

Dear Sir: I have just read Dr. Herbert Inhaber's very interesting article, "A Canadian view of monitoring activities," (*ES&T,* March 1975, p 206). This article represents an excellent example of the use to which the Smithsonian Institution's data on pollution monitoring programs can be put.

I should like to bring to the attention of your readers that the *Directory of National and International Pollution Monitoring Programs,* published by the Smithsonian Institution in 1974 under contract with the United Nations Environment Program substantially is out-of-date. However, we have maintained a computerized data base on worldwide pollution monitoring programs that now contains information on the operational and administrative characteristics of 700 existing monitoring programs in 78 countries and territories. A printout of this up-to-date information is available in a directory format at cost from the Smithsonian Institution, Center for Short-Lived Phenomena, 60 Garden Street, Cambridge, Mass. 02138. The data base itself also is available on magnetic tape.

John Whitman, Program Manager
Smithsonian Institution
Office of International and
Environmental Programs
Cambridge, Mass. 02138

Small particles

Dear Sir: Is there a microparticulate mechanism in heart/lung disease? A major medical effort is taking place to locate the source of the lung cancer and coronary disease epidemic in eastern Finland. For example, in that region, lung cancer affects over five times as many males as it does in Norway. And the heart disease rate is the highest in the world! We might be closer to a solution through the research on stack emissions from coal-fired power plants (*ES&T,* November 1974, p 1107) in which toxic concentrations of trace elements were found to increase sharply with decreasing particle size.

Microparticulates on the order of the wavelength of light bypass not only the stack filter but also the body's respiratory filter. Thus, the almost invisible aerosol haze suspended above cities could well prove more deadly than the heavy sulphur-laden smog that sets emission standards. Ironically, if a fossil-fuel power plant severely limited its SO_x emissions, it could thereby operate at higher levels and in so doing release higher concentrations of toxic aerosols.

There are few smokestacks of this type in eastern Finland to foul the country air. However, a similar plant stands in the backyard of nearly every Finn—a wood-burning sauna. In eastern Finland particularly, the open-fire sauna, presmoked before entering, is an almost daily way of life.

One would think that the sauna, or for that matter any extensively used indoor wood or coal fire, would top the list of prime suspects. But Fradley Garner, international editor of *Environment,* has long maintained that the Finns have avoided a determined search for a possible correlation between the sauna and heart and lung disease. Garner has authored an anthropological study of sauna habits, particularly in Finland where the sauna is sacrosanct.

The stack research introduces a plausible mechanism. The sauna environment differs in one important aspect from the surroundings of a smokestack. In a sauna, conditions are far from ideal with respect to the ability of the human system to resist overloading such as might come about by a massive intrusion of microparticulates.

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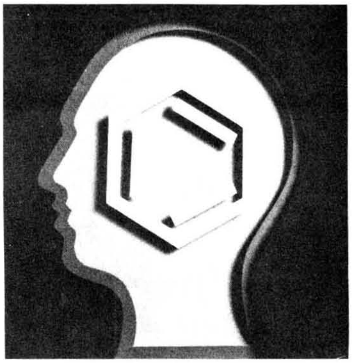

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For author's guide and editorial policy, see June 1975 issue, page 547, or write Katherine I. Biggs, Manuscript Reviewing Office, *ES&T*

Sludges: there are options

This is a turbulent time for sludge processors. What to do with sludges, the man-made by-products of 20th century technology, has plagued managers of industrial operations since the 20th century began. Presumably, if and when viable solutions appear for this age-old dilemma, all would start using them. Well, a number of processes are available; many of them are discussed in an outlook story.

The choices take a number of different forms. Some are throwaway processes. Here the oozing materials are immobilized, put in place in landfill or used in construction activity or roadbed preparation. Others are reprocessing processes. Here, as in the PAT report, sludge materials from an industry are reprocessed, and the recovered valuable material(s) is put to use right back in the industrial operation that generated the sludge material in the first place. The last and perhaps futuristic approach is reprocessing and reconversion of the material for use in a different industry from that in which it was generated. Here, for example, would be the reconversion of electric utility scrubber wastes being changed into fertilizer material.

Already, some are beginning to refer to these approaches as first generation, second generation, and third generation sludge processes. A number of processes in each of the three categories is available. Obviously, the hurdle in the use of any sludge processing technology is economics. No matter what happens, one has to pay for whatever one does to sludge. Whether one pays in the transportation charges—assuming that the landfill or company site is available—or treatment, these are the choices.

It would seem that sludge conversion faces an uphill struggle similar to that of its "poor relation" environmental cousin, resource recovery. Some environmental watchers foresee an end to this sludge processing dilemma in the near-term. Others stand back and observe. To all we can only comment, get in there and do something about it in your daily industrial activity!

Stanton Miller

Problems can be opportunities in disguise.

The twin dilemmas of energy and the environment may, in the long run, provide man with his best chance to reassess some old assumptions and reorder his priorities for a safer, more pleasant life.

Even before these problems reached crisis proportions, Chiyoda—Japan's leading engineering firm—was developing technology that will help ensure both environmental integrity and efficient energy production.

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CURRENTS

INTERNATIONAL

A Centre for Studies on Environmental Monitoring and Assessment is being established at Chelsea College, University of London, under the direction of Prof. G. T. Goodman. A project initiated by the Scientific Committee on Problems of the Environment (SCOPE), developed and coordinated by the Centre, and funded by the U.N. Environment Program and others will cover four major study areas: monitoring data characterization; variations in monitoring requirements; the dose commitment concept; and time perspectives of environmental change. The objective of the SCOPE project is to define, evaluate and solve significant monitoring problems of global, national and regional concern.

WASHINGTON

EPA denied a one-year extension of the Clean Air Act's 1975 deadline for controlling particulate emissions to three W. Va. electric power companies, citing bad faith efforts as the reason. The companies were the American Electric Power System (AEP) and two of its subsidiaries. At the same time, four other W. Va. power plants, including two of AEP's, were granted a one-year extension of the May 1975 deadline for controlling sulfur dioxide emissions.

New Dept. of the Interior regulations for exploration of the Outer Continental Shelf have been proposed. Geological and geophysical data obtained by companies while exploring for oil, gas and other minerals would have to be disclosed to the U.S. Geological Survey and the public under the new regulations. In addition, no permit to explore would be issued if the proposed operations harmed aquatic life, interfered with other users of the sea, or created hazardous conditions or pollution.

EPA's administrator Russell Train cited progress in meeting the primary ambient air quality standards that were to have been achieved by May 31, 1975, although he said ". . . there is still a long way to go." As examples of improvement he cited reductions nationally in the concentrations of sulfur dioxide, particulate matter and photochemical oxidants. In a status report to Sen. Edmund Muskie (D-Me.), Chairman, Subcommittee on Environmental Pollution, Train noted that 60 of the nations 247 air quality control regions (AQCR) would not meet standards for total suspended particulates by the statutory deadline; for oxidants, 74 AQCR would exceed the standards; and for sulfur oxides, 42 would not meet the statutory levels. Similar situations exist for nitrogen dioxide and carbon monoxide. Train felt that a sustained effort was still needed.

EPA's Train

NOAA's Deep Ocean Mining Environmental Study tentatively predicted the environmental impact of deep sea manganese nodule mining. The preliminary results indicated that the environmental effects, now largely unknown, would include stirring up sediments with the possible revitalization of long-dormant spores, and disturbing bottom life.

In another NOAA study, the ozone layer over the U.S. and Great Britain was found to have decreased by 2% from 1970 to 1974, but the annual rate of decline has slowed. The effects of thermonuclear explosions on the ozone layer were equivocal; volcanic eruptions and solar flares may alter the amount of zone, but the quasi-biennial oscillation in ozone makes interpretations difficult.

STATES

The Alabama Air Pollution Control Commission refused U.S. Steel Corp. a one-year extension to the May 1975 deadline of the Clean Air Act. The Commission would permit U.S. Steel to continue operating if it reduced its hearth emissions, and paid a token fine. Officials from the steel company said it was not corporate policy to pay fines, and the Birmingham hearth would probably be closed. In another Alabama city, Brewton, city vehicles have been converted to a dual fuel system to operate either on gasoline or compressed natural gas (CNG). CNG is a more economical fuel than gasoline, increases engine life, reduces maintenance costs, and virtually eliminates air polluting engine emissions.

In a recent decision, the Calif. Air Resources Board rejected plans to shut down industries, offices and recreational facilities during smog episodes. The Board claimed that there was no evidence that such a strategy would reduce air pollution during emergency periods. It did, however, resolve to develop a plan to protect sensitive individuals during smog episodes.

States battle the bottle ban. In a straw poll taken by NBC-TV-Chicago, Illinoians voted almost 4 to 1 against enactment of a bottle bill patterned after Oregon's legislation (*ES&T*, November 1973, p 1000). In an Associated Press survey of Idaho's legislators, more than 63% opposed a bill similar to Oregon's ban on nonreturnable beverage containers. The lawmakers felt that it put the burden on the small retailer without attacking the total litter problem. On the other hand, Vermont has strengthened its law by mandating that all glass containers must be refillable, prohibiting "flip-tops" on cans, and placing a five-cent deposit on all beverage containers.

New York and Michigan have designated the National Sanitation Foundation's Water Quality Index as the index number to use in compiling their annual water quality inventory reports to Congress, via transmission to the EPA, as mandated under P.L. 92-500. The index was developed with the assistance of more than 100 scientists who selected nine major index parameters to be used to characterize water quality. Among the parameters chosen were dissolved oxygen, fecal coliform bacteria density, temperature, turbidity and various undesirable chemicals. These parameters, by themselves or in combination, aid the water quality expert in determining whether water is safe for human consumption or surface body contact, and whether the body of water will support fish and other aquatic life.

Phoenix, Arizona, has instituted an emission inspection and quality control program for its 3500-plus vehicles. The

Arizona monitoring

system was designed and its main component supplied by Automotive Environmental Systems, Inc. (Westminster, Calif.). Within the first nine months of operation over 2,500 full inspection tests have been run. In addition to minimizing emissions from the fleet vehicles, more than a 10% reduction in fuel consumption has been realized; the quality of maintenance has improved substantially; the number of vehicles failing in the field has been reduced significantly; and the number of vehicles returned by the user after preventative maintenance has been reduced.

Two scientists associated with Michigan State University have found that coliform bacteria, normally found in human intestines, can also live and reproduce outside the human body. Traditionally, coliform bacteria have been indicators of sewage contamination of water, but with this new finding, bacteria counts may no longer be accurate indicators of pollution level.

California's State Water Resources Control Board, the Dept. of Water Resources, and the Dept. of Health have established a panel of experts to help develop the data needed to establish water reuse criteria to protect public health. The State Water Resources Control Board is charged with cleaning up municipal wastewater, reuse of which would relieve pressure on California's limited supplies. The Dept. of Water Resources is interested in a comprehensive management program coordinating impounded supplies, surface waters, groundwaters and reclaimed wastewater. The Dept. of Health is charged with setting standards for wastewater reuse in such areas as direct reuse, recreational use, groundwater recharge and irrigation.

MONITORING

Measuring traces of toxic metals in wastewater is accomplished with a flow-through electrode system developed at the University of Wisconsin-Madison. The system responds to copper ion concentrations as low as one part per billion (ppb), far below limits of conventional dipping electrodes. Prof. Walter Blaedel, the system's developer, believes that the flow-through electrode could be used in a compact, portable analyzing instrument, rather than in sophisticated laboratory equipment presently needed for ppb measurements. The system is basically a pencil-shaped electrode inserted in a thin tube where the water flows. Ion concentration in the water is related to electrode voltage.

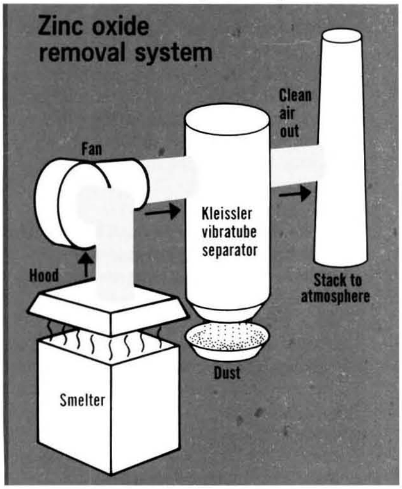
Two new standard reference materials (SRM) for mercury in water are the first nonradioactive water pollution standards developed and offered by the Dept. of Commerce's National Bureau of Standards. SRM 1641, concentrate, and SRM 1642, trace, are certified for mercury at levels of 1.49 ± 0.5 ppm and 1.18 ± 0.5 ppb, respectively. SRM 1642 encompasses EPA's primary standard for mercury in drinking water, 2 ppb.

TECHNOLOGY

Disposal of difficult-to-treat wastewater may be aerobically treated by ICI's Deep Shaft process. The Deep Shaft could be as much as 500 ft deep and 32 ft in diameter, and lined with steel or concrete. In fact, the shafts are concentric, and wastewaters are concentrated there, where air is driven in to be the main nutrient for the waste-consuming microorganisms. Liquid wastes go to the shaft bottom and then up the sides where they meet the air. Available oxygen increases because of higher pressure. Retention time is about 2 hrs (normal activated sludge retention time is 8–12 hrs), and land requirements are modest. ICI operates a 426-ft deep pilot model made in England.

Flue gas desulfurization without risk of incrustations, hard scales, and soft pluggages in the SO_2 removal system is possible when chloride ions (Cl^-) are added to the lime scrubbing medium. The Cl^- ions are used in Hölter process developed by Saarberg-Hölter Umwelttechnik GmbH (Saarbrücken, W. Ger.). Flue gas temperature is reduced, and the gases are washed in "Rotovent" rotational venturi stages. Dust and SO_2-laden fluid are then centrifuged out, and demisting takes place. The Cl^- ions insure better calcium bonding to sulfur radicals; oxidation to gypsum is then accomplished. Efficiency is over 80%, and often as high as 95% in 40 MW pilot plants.

Effective removal of troublesome zinc oxide emissions with a dry collection system was announced by the G. A. Kleissler Co. (Edison, N.J.). Zinc oxide, with fine particles, is difficult to handle, but the company solved the problem with a large separator with an extremely low air-to-cloth ratio. This combination helped to offset the static electricity generated by zinc oxide particles, and diminished problems in the tube walls caused by statically



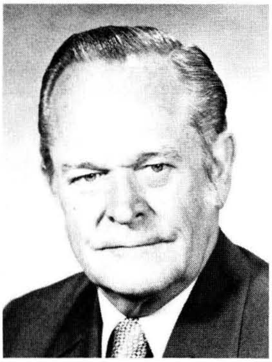
charged zinc oxide sticking. A careful choice of cloth filter porosity is of the essence. Recovery of up to 100 lbs/day of marketable zinc oxide is achievable, and downtime is essentially limited.

High-performance incineration of liquid residues and sludges is possible with the CINCLUS mass combustion process developed by Societe ELF-UNION (Issy-les-Moulineaux, France). The process uses a Multifluid Burner, which takes combustible fluids, high-pressure air, and combustion air, as well as harmful or malodorous gases to be destroyed. The undesirable materials are injected into the heat source after they are emulsified in the burner head. NO_x emissions are inhibited and fuel consumption is reduced because combustion temperature is low (800–850° C, as a rule). The process destroys paper mill liquors, bacteriological effluents, cyanide baths, phenolic effluents, and many other noxious wastes.

Removal of heavy metals from waste streams is sufficient to meet the 1.0 ppm requirement for copper. At the same time, a marketable (or readily disposable) by-product becomes available through a process called extended-surface electrolysis (ESE) developed by the Engineering R&D Division of Du Pont. Essentially, ESE uses a spiral-cell "jelly-roll" construction rather than the usual planar electrode arrangement. The ESE system is inserted into a pipe, and has void volume of 93–95%, thus providing low fluid flow resistance. Efficiency, in this case of copper removal, becomes 100% at concentrations of 100 ppm or more, and is high even at 10 ppm. Work is proceeding on other heavy metals, and shows promise.

The "most advanced electric vehicle in the U.S." was unveiled by the Copper Development Association Inc. (CDA, New York, N.Y.) in Washington, D.C., in May. Called the "Copper Electric Town Car", it has a range of 120 miles and a top speed of over 55 mph. Cruising speed of the frontwheel drive car is 40 mph, and the range in stop-and-go city driving is 75 miles. Energy fuel costs for the car, based on present electricity costs, are estimated at 2–3¢/mi. Car weight, including about 1200 lbs of batteries, is 2952 lbs, according to CDA, which predicts that weight will decrease as battery technology advances. The 18 six-volt lead-acid batteries can be recharged overnight on 220 V ac from total discharge.

Alan Loofbourrow, vice president, engineering, of Chrysler Corp., told the Democratic Forum (Washington, D.C.) that his company pledges to increase automobile efficiency by 40%, on a sales-weighted basis, by 1980, and can do so if emission rules are held back sufficiently to allow an effective efficiency and emission control technology to be brought about by that year. As for cutting private car use, Loofbourrow said that free market pressures should accomplish this goal, and that undue forcing of vehicle use reduction could cost 150,000 jobs in the auto industry, as well as 500,000 jobs in related industries.



Chrysler Corp.'s Loofbourrow

Ford Motor Co. hopes to start a study on the use of a 100-hp version of a Stirling external combustion engine (first invented in 1816) for use in Pinto-sized cars. Meanwhile, Ford is testing a 170-hp Stirling engine in a 1975 Torino in Holland under contract with N. V. Philips, and plans to ship the car to the U.S. before the end of this year. A Ford official sees potential adventages over a comparable-size internal combustion engine in low emissions and greater efficiency. With the 170-hp Stirling, hydrocarbon emission was 0.1 g/mi; carbon monoxide, 0.31 g/mi; and NO_x, 0.4 g/mi, well below 1978 U.S. requirements of 0.41, 3.40 and 0.4, respectively.

Thomas Carmody, a vice president of Union Carbide Corp., asked scientists to make clear distinctions between fact and supposition when they discuss emotion-laden health issues. One such issue is in the finding of trace amounts of substances—which may or may not prove harmful—in the air; this poses a question whose answer may come after years of patient research. Carmody noted that in discussing such issues, scientists recognize the element of speculation, but the media often do not, and thus the press often takes speculation for fact. This, in turn, stirs public alarm and activist pressure for fast governmental action even though a real problem was not defined, he said.

Frost & Sullivan, Inc. (F&S, New York, N.Y.) **sees the water pollution control (wpc) market in Japan** increasing from $873 million to $3.4 billion by 1980; this represents a 21% average annual growth. About 500 companies are in the pollution control industry in Japan now; in the next few years, this figure could be 700. The highest rate of growth—51% annually over 1973–1980—will be enjoyed by companies in sewage sludge handling and treatment equipment, according to F&S. Current capital expenditure on wpc in Japan is about 24% of the total $1.7 pollution control investment; that 24% should hold when the total increases four times by 1980.

To meet 1983 pollutant levels, the steel industry will have to expend $12–14 billion on new pollution control equipment during the next nine years. The study by Arthur D. Little, Inc. (ADL) for the American Iron and Steel Institute (AISI) covered 130 plants, about 94% of the U.S. steel making capability; it analyzed the economic impact of pollution control costs on a plant-by-plant, product-by-product basis. The central problem facing the steel industry, according to the report, is one of capital availability. The total capital requirement through 1983 was estimated at $48–50 billion (1975 dollars), of which $21 billion will be needed to modernize existing facilities and $15 billion to increase annual steelmaking capability.

OUTLOOK

Ozone can help clean water and air

Some people never seem to get the word! The "word" is the often-heard statement that the use of ozone to decolor, depollute, disinfect, and deodorize water and air is uneconomical. Apparently it never reached Montreal (Canada), where the Charles J. des Baillets Water Filtration Plant is being constructed. That plant, whose estimated cost is $500 million, will ultimately be the world's largest of its kind, and will process 500 million Imperial (about 600 million U.S.) gpd, with a total production of 15,000 lbs/day of ozone.

This giant treatment plant and other pertinent topics were discussed at the Second International Ozone Symposium, held at Montreal in May, and organized by the International Ozone Institute (IOI Waterbury, Conn.), of which Morton Klein of Illinois Institute of Technology Research Institute (Chicago) has recently been elected president. Formally founded in 1973, the IOI seeks to bring together engineers and scientists in many disciplines in order to advance ozone technology and applications, and to dispel numerous erroneous beliefs concerning ozone. Perhaps to underscore the sharply renewed interest with which ozone is being regarded there were, among the approximately 500 symposium attendees from numerous countries, people of the stature of M. Jean Hallopeau, director of the huge Compagnie Générale des Eaux (CGE, or General Water Co., Paris, France), who participated actively in the symposium's deliberations.

Drinking water

In his welcoming address, Prof. Marcel Gagnon of the University of Québec at Montreal (UQAM), the symposium president, stressed the need to promote scientific interchange concerning the possible solutions that ozone might bring to numerous environmental problems, such as those of air, water, and wastewater, and to related medical and biological problems. But what are some of these problems?

One such problem is that of clean water. This problem was suddenly worsened over the last several months by the suspicion that drinking water at New Orleans, La., and at numerous other U.S. cities, contain carcinogenic compounds. To add the proverbial icing to the cake, there are now fears that chlorine, widely used in the U.S. to process drinking water, contributes to the formation of these undersirable compounds through combination with artificially or naturally formed organic chemicals in the water. Moreover, in some quarters, chlorine's disinfection—especially viricidal—efficacy is being called into question, as far as drinking water disinfection dosages are concerned.

Does the use of ozone attack this problem meaningfully? Two ozone-using drinking water treatment plants, the only two in the U.S., at Strasburg, Pa., and Whiting, Ind., may provide some insight as to how well ozone can work.

EPA carcinogen suspect list

Bromochloromethane
Bromoform
Carbon tetrachloride
Chloroform
Dibromochloromethane
1,2-dichloroethane

Strasburg, Pa., near Lancaster, draws its water from 13 mountain springs. Ozonation is the sole treatment. IOI technical director Rip Rice informs *ES&T* that Strasburg's water is of "very high quality," even though no pre- or post-chlorination is done.

Whiting, Ind., just outside Chicago, however, may be a more pertinent case in point. On the south shore of Lake Michigan, Whiting takes its water from an area next to some of the largest petroleum refineries, petrochemical complexes, steel mills, and sewage treatment plants in the world. Indeed, Whiting's intake water from Lake Michigan first goes through a petroleum refinery (though it is not a refinery by-product) where it receives a small amount of pre-chlorination. The water is then ozonated at Whiting's drinking water plant, to destroy organic materials that cause odor and taste problems on subsequent chlorination. The next steps are flocculation, pre-chlorination, sand filtration, post-chlorination, and distribution.

Typical analysis revealed that Whiting's water had 0.5 μg/liter of chloroform and 0.3 μg/liter of bromodichloromethane; the four other chlorinated organics on the U.S. EPA's carcinogen suspect list were not found. Pre-chlorination at the refinery might explain what chlorinated organic presence there was. Strasburg's water shows less than 0.1 μg of chloroform, and none of the other five EPA suspect substances.

How does ozone work in tandem with activated carbon? The Canadian Department of National Health and Welfare plans to run exhaustive tests on ozone/carbon/post-chlorination drinking water plants at Québec City, Canada (of which there are 20), in order to find out.

Toxic effluents

Ozone can have a devastating effect upon molecules of many toxic substances. Particular cases of interest involve highly toxic phenol and chlorophenol wastes. C. Nebel of Welsbach Ozone Systems Corp. (Philadelphia, Pa.) reminded the symposium that only 2.5 ppb of phenol can adversely affect water taste and fish flesh; higher concentrations can kill everything in a stream. Also, chlorination of phenol-laden water will form even more toxic chlorophenols, Nebel pointed out. An idea of phenol's toxicity may be obtained if one holds a small crystal of phenol in the palm of his hand for about one-half hour. At the end of that time, a blister should be formed.

The Molson brewery (Montreal) had an orthochlorophenol problem in its effluent. Nebel explained that Molson now treats 100 gpm with 2 lbs/day of ozone. The capital cost was $9950, and operating costs are about $2/day; the pollutant is satisfactorily destroyed. On the other hand, a Canadian paper mill needed to invest $260,000 and incur $60/day operating expenses to decompose phenol wastes in its effluent. For a plant with a bad COD problem as well as with phenol, Nebel estimated a $200,000 capital investment plus about $100/day operating costs.

Ozone also seems to be effective in destroying sulfides, cyanides, and thiocyanates, as well as pesticides and other objectionable substances. Metals, such as iron and manganese can be oxidized with ozone and subsequently hydrolyzed and precipitated. In the cases of certain refractory toxic organics, biodegradable organic compounds can be formed.

Odor removal

While ozone is thought of mainly in terms of water treatment, it has air cleanup functions as well. For example, Hitherto unrealized problems with some "conventional" techniques are stimulating revived interest in this old-new method of treatment and pollution control

Largest drinking water ozonation plants[a]

Location	Water flow (m^3/day)	Ozone output (kg/hr)
Montreal, Canada[b]	2,300,000	300
Moscow, USSR[b]	1,150,000	200
Choisy-le-Roi, France	900,000	115
Neuilly-sur-Marne, France	600,000	120
Manchester, England	480,000	50
Kiev, USSR	400,000	80
Gor'kiy, USSR	350,000	30
Orly, France	300,000	50
Mery-sur-Oise, France	300,000	45
Łodz, Poland	290,000	40
Chiba, Japan	270,000	38
Brussels, Belgium	250,000	25
Singapore	230,000	48
Wrocław, Poland	180,000	17
Amsterdam, Holland	125,000	25
Toulouse, France	55,000	17

[a] Partial list; [b] Under construction or planned;
Source: Trailigaz, Compagnie Générale de l'Ozone (Garges-Lès-Gonesse, France).

K. Reither of Kunststoff-technik KG (Troisdorf, West Ger.) told the symposium about a transportable pilot plant for odor removal, based on techniques developed by the Fresenius Institute (Wiesbaden, West Ger.).

The system was tested at an aluminum plant where ozone is introduced into exhaust air at 2–19 g/hr. Final air exhaust contains less than 1 ppm of ozone. The amount of gas throughput to be treated with ozone is about 50,000 m^3/hr. Odors are reduced by 90–99%.

The system is essentially a recycling arrangement with two stages. The first stage receives 0.1–0.3 ppm of ozone with a 10% aqueous sodium hydroxide solution wash. The second stage takes 0.5–1.0 ppm of ozone and a mild acid wash. Contact time in each stage is normally 2 sec. The capital cost of a treatment system was estimated at $165,000, with operating costs of $8/hr, based on a working week of 120 hours.

Exhibits

An integral part of the IOI symposium was the equipment exhibit. Over a dozen companies from the U.S., Canada, and France were represented.

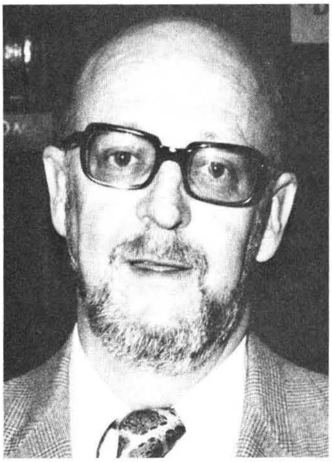
One exhibit showed the "Sonozone" ozone/ultrasonics system for treating sewage, which Telecommunications Industries, Inc. (Lindenhurst, N.Y.) has installed at Indiantown, Fla. (*ES&T*, June 1974, p 493). Another by Ozonair, Ltd. (Montreal) involved a system by which the water is introduced into the ozone, instead of vice versa, as is normally done. Ozonair president Karel Stopka told *ES&T* that when his system is in "full swing", water, even sewage, could be cleaned with reduced energy use, and with a contact time of only 12 sec (at the Montreal plant, contact time is to be 8 min). Welsbach and W. R. Grace (Columbia, Md.) exhibited, as did Canadian Waterworks & Ozone, Ltd. (Canozone, Montreal); Canozone will build the ozone treatment system for the giant Montreal water treatment plant. Degrémont (Reuil-Malmaison, France), one of the world's large environment firms, represented France and showed a horizontal-tube ozonator system for water purification.

Reduction to practice

One person following ozone technology very closely is Victor Goldbloom, minister of municipal affairs and environment of the Province of Québec. He told the IOI symposium luncheon session that he would like to see pilot and demonstration projects reduced to practice as soon as it is practically possible. Goldbloom also estimated that because of new problems coming to light with respect to water and the substances it may contain, accelerated development work in the field will ensue, and will lead to breakthroughs relatively quickly.

Perhaps one such breakthrough may be at hand with regard to methodology. For instance, Rist-Frost Associates (Laconia, N.H.) are finding that with activated carbon filtration, followed by ozonation and then post-chlorination, operating costs of drinking water treatment may be reduced by about one-third, as compared to "conventional" chlorination. Viral kill is still brought about. Interestingly enough, Quebec City ozonates prior to activated carbon filtration, whereas the reversal of these two steps at Laconia, N.H., seems to have been a cost reduction factor.

Be that as it may, prospects for sharply increased use of ozone could be bright, especially in view of the latest developments concerning potentially dangerous substances and viruses in water. Hopefully, the technological breakthroughs that Minister Goldbloom foresees will come to pass, and the "word" that ozone treatment is not economically or technically feasible will be relegated to the myth file. JJ



Symposium president Marcel Gagnon
"Solution through idea interchange"

CGE director Jean Hallopeau
"Long experience with ozone"

As consumers organize, and industry begins to feel the economic pinch of pollution control laws, litigation may increase as will the need for

The expert witness

On the rain-soaked grounds of the Williamsburg (Va.) Convention Center, the nation's toxicologists recently met to hear the latest scientific and technological advances in their field. Sessions covered the full spectrum of interest to a toxicologist:

- the metabolism, toxicity, and mechanism of action of substances in organs, tissues and cells
- the carcinogenicity (cancer causing), teratogenicity (abnormal growth or fetus formation) and mutagenicity (mutation inducing) of drugs, pesticides and general chemicals
- the methodologies, including new ways to use established instruments or procedures
- the toxicologist as expert witness.

The session on the expert witness examined the role of the toxicologist in adversary proceedings, both public (regulatory hearings) and judicial.

As society has benefited from the production and marketing of ever-increasing numbers of new products so, too, has it suffered from mishaps that occur during the manufacturing process, and from the use of the finished product. The person injured in the mishap may seek compensation: enter the lawyer and the expert witness.

On still another front, industrial and manufacturing processes, unless properly controlled, may pollute the environment. To curb pollution of the air, water and land, legislators have promulgated laws, the economic implications of which are being felt more strongly by affected industries. As these industries begin to react to stem the tide to reduce the costs involved in complying with these regulations, the need for the expert witness should, if anything, increase.

In his introductory remarks, Dr. Charles Hine of the University of California Medical School noted that in the disposition of disputed issues, the scientific community has a substantial, indispensable role to play in the administration of justice. The expert witness, with integrity and impartiality, must guide the trier of fact—the hearing body, judge or jury—to reach a just determination in a case.

The expert need not be, but in most cases is, a scholar or a specialist in his field; the question of the witness' qualification is usually at the discretion of the judge. However, most lawyers prefer to err on the side of over-qualification and to select their witness(es) on the basis of academic credentials and professional experience. Recruitment normally occurs from the ranks of academic faculties, retired government or industry personnel, consulting engineers and authors of technical publications.

Functions, preparations

The functions of the expert witness are many. Before the adversary proceedings, the expert can "educate" the lawyer about the technical details of the case and, thereby, aid the lawyer in his preparation of an effective trial strategy. The expert now begins to collect the data, analyze existing data sources, and make recommendations to the lawyer for additional research or testing. In conferences with the lawyer, the expert witness carefully prepares his direct testimony in simple, direct language so that its articulation in court is not confusing.

At trial his role is twofold: to give testimony on his interpretation of the evidence to the trier of fact, and to give technical advice to his lawyer.

Before the trial or hearing, the area of expertise of the witness must be carefully defined and delineated, by the lawyer and by the witness himself. To stray beyond his area of competence on direct examination may land the witness, during cross-examination, in very hostile territory indeed.

Usually, the expert witness will be brought in for conferences with his lawyer before the actual proceedings. In these conferences, the lawyer will be informed of the scope of his witness' testimony *before* the proceedings, and the expert can be apprised of areas of his testimony fertile for questioning during cross-examination. As was emphasized again and again by the three lawyers—no lawyer wants to be surprised by his own witness. Further, these pre-trial/pre-hearing conferences are not coaxing sessions so much as coaching sessions to help the witness give more competent answers to questions put to him, and, in turn, aid the trier of fact to arrive at a just decision.

The regulatory agency

Dr. Albert C. Kolbye, Jr., associate director for sciences in the Bureau of Foods within the Food and Drug Administration, defined the role of the toxicologist as expert witness within the special framework of a regulatory agency, which he also defined. The regulatory agency, part of the executive branch of government charged with issuing regulations and interpreting these when they come into dispute, has functions that fall partially within the legislative and judicial provinces.

The powers of an agency are counterbalanced by legislation passed by Congress and by its appropriations power. The courts offer judicial restraint that assures that an agency does not exceed its statutory authority, that it observes due process in proceedings, that its actions are within its limits of discretion or a matter of record based on evidence, and that it does not act in an arbitrary or capricious manner. The public, public interest advocates, technical experts and the scientific community in general also exert degrees of influence on the actions of a regulatory agency.

When agency policy is questioned or a decision contested, administrative hearings, with the right to cross-examination, are held. Here an expert witness, qualified by training and/or experience, can render an opinion on the issue(s) in dispute. His qualifications and credibility as an expert will be challenged by opposing counsel during cross-examination. Therefore, an expert witness should remain within his scope of expertise.

Toxicologists have historically testified in cases involving forensic toxicology or forensic pathology. According to Kolbye, a far more difficult arena for both the regulatory agency and the toxicologist is the area he terms "preventive toxicology" sans dead bodies or poisoned people. Here, the legal aspects are cloudy and remain largely to be explored. But the toxicologist as expert witness can deliver his honest opinion and the basis for it, and in this manner absolve his obligation to advance knowledge.

The lion's den

Jerome Heckman, senior partner in the Washington, D.C., law firm of Keller and Heckman, with wisdom and humor dispensed advice to the scientists on their role and conduct in hearing and judicial proceedings.

For attitudinal settings, Heckman noted that the toxicologist should first try to understand the type of proceedings he is to become involved in, and then tailor his preparation for that type. Further, he should know who will be receiving and weighing his testimony, which can influence his mode of presentation. And finally, the toxicologist should prepare intensively for effective cross-examination by a "devoted and able advocate."

The uniqueness of expert testimony is that although it is an opinion and may be disbelieved or given no evidentiary value by the hearing body, judge or jury, it must be accepted as valid testimony of record. Therefore, the expert witness must establish his area of expertise by reciting his credentials—education and experience. He then should state his professional opinion and his reasons for it. His testimony should be given in nontechnical, jargon-free language, and should progress in a logical manner. Heckman cautioned strenuously that "To assume that the listeners know any of your basic premises, or to skip any step in an explanation can make your testimony useless."

The testimony must show that in the opinion of the expert, the result(s) did or will emanate from the alleged cause. The requirement of professional opinion can be satisfied by words such as "I think" or "I believe," but it is best to use phrases such as "it is my professional opinion" or "this is my opinion" when testifying. Most importantly, the witness must reach a definite conclusion on the basis of the best available evidence, and his own best judgment.

When the expert enters the lion's den—cross-examination—he must be prepared to have his qualifications, integrity and sincerity, in short his credibility, questioned. He must be prepared for a strong challenge to the accuracy of his opinions. The best preparation for the crucible of cross-examination is just that—preparation. The expert witness should reread all authoritative treatises on the subject of testimony, for in addition to questions on his own testimony, the witness may be questioned on published theory and opinion.

Heckman advises thronged toxicologists

Upon taking the stand, the expert witness should listen carefully to all questions posed, answer only those questions, and only explain misleading interpretations, questions or answers. As cautioned in the military, the witness, unless a "courtroom pro," should never volunteer information.

The witness may be asked to compromise his expert opinion by admitting that another expert's opinion may have merit. He should remind his cross-examiner that he speaks as an expert on the basis of his training and experience. And further that "While, in general, reasonable men may differ, another man with (my) experience, knowledge, and expertise would not likely hold an opinion different from (mine) in the same precise factual setting."

Nitty gritty

After jokingly reproaching Heckman for giving *her* presentation, Theodora Gordon of Theodora Gordon Associates (Chicago, Ill.) talked about the techniques of being an expert witness: About how to enter into an adversary proceeding yet still emerge unscathed.

First, she stated that as a witness you the toxicologist will be chosen by a side that has a definite reason for choosing you. The lawyer choosing you wants to present the issues and the facts, but he also wants to win the case. So you will be picked for who you are, for what you are, for what you have to say and for where you will have to say it. Your lawyer will apprise you of the nature of the case, what you are expected to testify to, why you were called as a witness and what purpose your testimony will play in his overall strategy.

Your looks, mannerisms and speech are important: you must convey the image of competence and sincerity. The lawyer will most likely caution you on how to dress; usually the conservative image is best. When on the stand, if your manner is arrogant or argumentative, the effectiveness of your testimony will be destroyed, and it will be discounted.

Attorney Gordon reaffirmed the simple clear, concise approach to testimony preparation and deliverance. She also suggested that you as a witness not stipulate as to your qualifications. You've earned them, recite them—every last one of them!

Counter to Dr. Hine's view, Ms. Gordon felt that as a witness for the plaintiff, defendant or as a friend of the court, you will be testifying from a particular point of view, you will be a partisan. As she phrased it, "A witness without a point of view is nothing."

Perhaps the most important complement of advice she had to offer was that it was imperative that you understand the questions put to you, and that you take sufficient time to answer them. Answer completely, but don't rattle on interminably. Do not volunteer information. And, finally, stick to the norm, do not recite the unusual or abnormal occurrence.

And, with the words of advice that Heckman used to end his talk to the toxicologists, and with due apologies to the Book of Psalms, so, too, shall this article end. "Lo, though I walk in the shadow of the valley of the skeptic and cross-examiner, I shall fear no evil for integrity and knowledge are my staff. And, besides, I am the only man in this whole damn valley who really knows what all these data mean." LRE

The stabilization game

One of a series of anti-SO_x scrubber advertisements by a large U.S. electric utility, widely circulated last year, showed people and cities being slowly, but inexorably inundated by a vast pool of scrubber sludge of toothpaste-like consistency. In the caricature presented, a man was seen wading waist-deep through a sea of "goo" whose oozy waves were lapping at buildings and lampposts. A truly horrendous prospect!

Those who take delight in contemplating forthcoming catastrophes will be disappointed to learn that the "goo" flood will probably not occur. One reason is that a number of companies are now in business to process scrubber sludge so that it can go to making aggregate, to landfills, or to other uses, depending upon economic conditions in the vicinity of an SO_x scrubber.

Chemical approaches

One attack on the SO_x sludge problem is the Poz-O-Tec process being marketed by IU Conversion Systems, Inc. (Conversion Systems, Philadelphia, Pa.), a subsidiary of IU International Corp. Hugh Mullen, Conversion Systems' director of government and industry relations, told *ES&T* that the Poz-O-Tec process consists basically of two simultaneous reactions which take 48–72 hours. The first involves sulfate/sulfite alkaline earth compounds that may be present in scrubber sludge or added as needed; it produces a fibrous gypsum with low permeability and moderate bearing properties. The second consists of cementitious reactions, including pozzolanic reactions, between fly ash alumina/silica, lime compounds, and sulfur oxide salts. The technique of volume reduction of SO_x and fly ash sludges was essentially pioneered by Conversion Systems.

Calcilox is a patented chemical additive, developed by Dravo Corp. (Pittsburgh, Pa.), that turns sludge into a natural earth-type material with a particle size ranging between that of silt and fine clay. After two weeks, Calcilox-treated scrubber sludge (Synearth) achieves an unconfined compressive strength of over 4.5 t/ft^2; the compressive strength is the gradually applied load that a given solid material can sustain without fracturing or failing.

The principle employed by Research-Cottrell, Inc. (R-C, Bound Brook, N.J.) involves dewatering of the thixotropic (SO_x absorber) sludge, followed by mixing with dry fly ash to reduce free moisture further, and reduce overall disposal volume. According to R-C, cementitious reactions can occur among the components of sludge and fly ash without any additives.

Chemfix, Inc. (Pittsburgh, Pa.) uses a chemical fixation method based on soluble silicates and silicate setting agents. This method converts a wide range of liquid and sludge wastes into non-polluting, easily disposable solids.

Disposal or use

The dewatered product of Conversion Systems' Poz-O-Tec process has a number of possible uses. One use is as an aggregate substitute in Portland cement and bituminous concrete; blocks made with this aggregate meet specifications of the American Society for Testing and Materials (ASTM, Philadelphia, Pa.). Other uses could involve roadway, airport, and parking area paving; land reclamation and embankment construction; and dams and impermeable liners.

Suitability of the Poz-O-Tec product for landfills is enhanced by a permeability coefficient that can be as low as 10^{-6}–10^{-7}. This low permeability qualifies the Poz-O-Tec product as a "non-aquifying fill", since it is impervious, for purposes of civil engineering. Moreover, with this extremely low permeability, the product does not produce leachates in a landfill; indeed, it can be used as a bottom or top liner. Even trace metals and toxic materials are "locked up" within the product.

At present, the Poz-O-Tec system is in continuous use at a 160 MW power plant. This month, the system will have been in use for one year, and thus, have "proven itself" as far as scrubber sludge disposal is concerned. Conversion Systems' Mullen and executive vice president L. John Minnick estimated that with proper market conditions, a Poz-O-Tec system at a 200 MW power plant could support a conventional block plant.

Using sludge and fly ash. *Parking lot under construction*

In fact, the Poz-O-Tec system is an outgrowth of Conversion Systems' Poz-O-Pac system for utilization of fly ash in road-base materials, sub-grade paving materials, and soil stabilization. The firm has about 20 years of experience with Poz-O-Pac; a recent large-scale application of Poz-O-Pac was for the roadbed in the huge parking lot at the Three Rivers Stadium, Pittsburgh, Pa.

Dravo's Calcilox-Synearth system has been in use at a Duquesne Light Co. coal-fired power plant at Wireton, Pa., since the spring of 1974. The SO_x sludge is generated by four 125 MW venturi scrubbers. After two weeks in a curing pond with Calcilox treatment, the consistency is sufficiently workable for the sludge to be excavated and trucked to a nearby landfill.

Solutions to the problem of what to do with SO_x scrubber sludge are being sought and found

Starting this summer, however, Calcilox-treated sludge is to be slurried in a 7-mi long pipeline to an impoundment disposal facility in a natural valley. Stabilized sludge will be contained under water behind a 400-ft constructed earth and rock embankment, to be the highest such structure in Pennsylvania. After disposal operations are completed, the area could become a recreational site.

Next month, the Synearth system will start operations at a new 1760 MW Pennsylvania Power Co. station at Shippingport, Pa., with SO_x scrubbers expected to generate 21,000 tpd of sludge that the system is to process over the following 30 years. William Lord, a projects director for Dravo, estimates that costs for a long-term disposal system, from conception to final design and construction, would be on the order of \$2–4/ton of coal burned.

R-C expects to see its system in operation at a major southwestern utility's 1500 MW station in January 1977. The R-C system now in design will handle 1500 gpm (15% solids), and 3000 tpd of fly ash to give 4500 tpd of treated waste product. Equipment replication can provide increased capacity. Treated sludge will be used as a landfill or minefill. To date, however, R-C has operated only a 5000 lb/day pilot system for about six months. Nevertheless, the company believes that it has come up with a "technical and cost-effective solution" to the SO_x sludge problem, and that market acceptance will come with this full-scale demonstration.

Since 1971, the Chemfix process has been converting various sorts of sludges into non-toxic, non-polluting mineral matter. Du Pont, Exxon, Ford, Sun Oil Co., and SOHIO have been among Chemfix customers, as has the City of Indianapolis, Ind. Also, on a demonstration basis, the Chemfix system is in use at TVA (Paducah, Ky.) and Commonwealth Edison (Joliet, Ill.).

Permeability coefficients

10^{-6} Water takes one year to penetrate 1 ft thickness[a]

10^{-7} Water takes one year to penetrate 10^{-1} ft thickness[a]

Materials with permeability coefficients of 10^{-6} and less are considered impervious for civil engineering purposes.

[a] Based on material being constantly wet.

Larry Gowman, vice president of development for Chemfix, estimates that his company's volume of business for this year will be \$3 million in this field. He told *ES&T* that Chemfix systems have handled up to 150,000 gal per 10-hr day of sludge, which is then disposed of on land. He sees future prospects for system sales and customers as being dependent upon regulatory law and its enforcement.

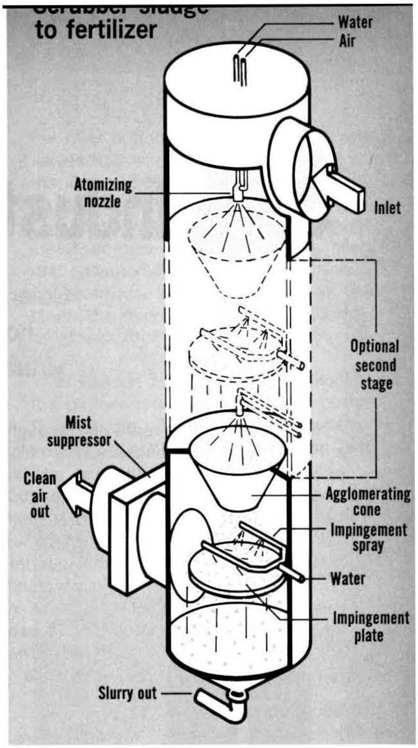
Other developments

This year, Ralph Peck of Illinois Institute of Technology (IIT) and Ladd Pircon, president of Purity Corp. (Elk Grove Village, Ill.) have announced a process to convert SO_x scrubber sludge to high-quality chemical fertilizer. The SO_x emissions from high-sulfur Illinois coal, for example, combine with other chemicals injected into the exhaust stack, and produce a fertilizer that can be used in liquid state, or can be dried and granulated for spreading.

First small-scale attempts to make this fertilizer used potassium carbonate as the injected chemical; later, anhydrous ammonia, and finally, phosphate rock were tried. Efficiency of SO_x removal fell to 90% only after many hours of continuous recycling of liquids used in the process. Opacity at the stack never exceeded 6%. The IIT-Purity Corp. pilot plant was designed to burn 200 lbs/hr of coal, and handle 2000 ft^3/min of exhausts produced. The object is to produce fertilizer in lieu of sludge.

At the University of Toledo (Ohio), Donald Angelbeck, David Colony, and Ronald Watt are finding that municipal water filtration plant waste sludge can increase unconfined compressive strength and leachability resistance of lime-fly ash-graded aggregate (LFA) pozzolanic pavement material. Such LFA material could conceivably be derived from scrubber sludge.

Scrubber sludge to fertilizer



If the LFA plus water sludge are cured seven days at 100°F, it achieves a 50% higher compressive strength than does LFA without the water sludge. Also, 12 cycles of freeze (−35°F) and thaw, according to the ASTM C-593 testing method, showed 14% higher LFA strength than did a standard LFA mix.

Perhaps the volume of SO_x sludge from a limestone scrubber can be reduced at the source. M. W. Kellogg Co. (Houston, Tex.) claims that its horizontal stack gas scrubber (*ES&T,* January 1975, p 18) cuts waste sludge slurry volume by 50% and yields more pure gypsum. Kellogg adds a soluble sulfate—preferably magnesium sulfate—to improve slurry reactivity, and estimates capital costs for a 540 MW system of its construction at \$55/kW, with add-on power costs at 0.354¢/kWh.

The worst is not to come

In view of the possibilities of useful disposal or recycling of scrubber sludge products, or eliminating sludge altogether, through technology existing or to come, the gigantic "goo" inundation, of which the major electric utility warned, will probably not happen. Other arguments—perhaps valid, perhaps not—might be made against SO_x scrubbers; for example, concerning cost-effectiveness, efficiency, technical capabilities, and the like. But the prospects of the U.S. drowning in a viscous sea of sludge may be considered remote. JJ

Steel industry sludge is being reused

Colerapa Industries takes waste from a mill's hot strip-rolling operation and recovers virtually all of the iron value for reprocessing

All steel mills put steel slabs through a hot strip-rolling process. On a daily basis, valuable iron units are lost in every facility in the world. Typically, 100 lbs of raw material charged to a steel mill winds up as finished product (75%) and waste (25%). Of the latter quarter percent, 22% ends up as slags, and there are many companies that are in the business of reprocessing these slags for further use in steel mills. The remaining 3% are sludges—mill scale.

The problem

Throughout the hot strip-rolling process, the slab, sheet, bloom, billet, or bar is being oxidized, cooled and washed with a high pressure water spray. When the hot steel is exposed to oxygen in the air as well as the wash water, a layer of iron oxides is formed on the entire surface of the steel as it is being rolled. This layer of oxides is called mill scale or simply scale.

As the steel is rolled, this layer of scale is broken away and replaced by a new layer. This generation of new scale occurs each and every time the size or shape of the hot steel is changed.

As the scale is broken away from the steel, it falls through the roll tables into a flume or sewer through which high velocity water is flowing. In addition to the scale and water, a large amount of lubrication greases and oils from the rolling machinery as well as other mill debris find their way into the flume or sewer. The scale, water, grease and oil combine to form a sludge.

This sludge poses a serious water pollution problem if it is discharged into a waterway. In order to control this pollution threat, settling pits and basins are used to collect these sludges and thus prepare the water for reuse or discharge. Much has been done during recent years in the design and construction of these collection facilities to increase collection efficiency. In addition, terminal treatment facilities have been constructed and installed in an effort to upgrade the quality of water at the discharge from the conventional pits.

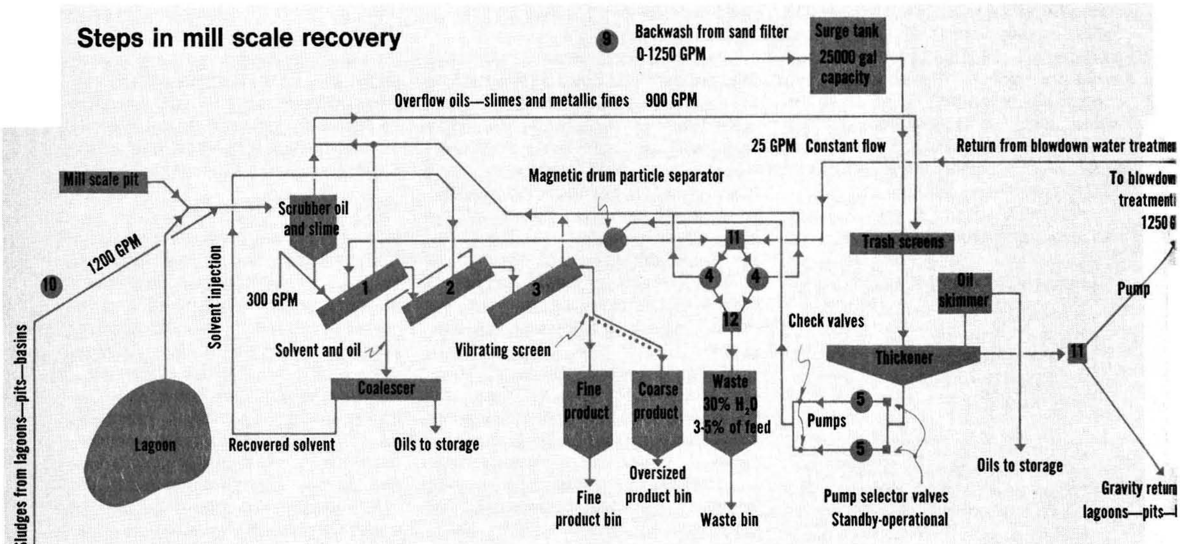
These terminal facilities include terminal lagoons and filtration units. However, as with any collection facility, the efficiency remains high only as long as the system is relieved of what it has already collected. Once collected, the sludge presents a double problem; how to relieve the collection facility and what to do with the sludge once it is removed.

Earlier practice

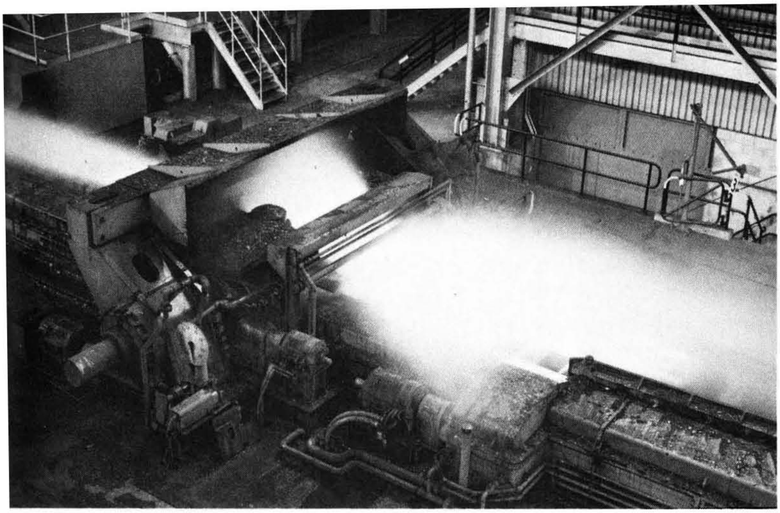
Traditionally, scale drags, ejectors, or mobile cranes equipped with a clamshell bucket were used to remove the sludge in the collection facility. In such practice, the larger solids are removed and trucked for reuse in the iron-making operation at the mill, while the smaller and more concentrated particles (which are more difficult to handle) found in the terminal lagoon and filter backwash are disposed of by dumping in land fills.

The required installation of air pollution control systems at agglomerating facilities in the iron-making operation has posed new problems involving the hydrocarbon or oil carryover. Thus, more of the total scale is unacceptable for reuse.

The basic concept used in the design of settling pits and basins is to create a quiescent body of water that slows the highly turbulent flume or sewer flow, and thus allow the waterborne solids to fall out of suspension, while permitting light oil fractions in the water to rise to the surface. Problems have arisen in the use of the traditional systems in that the quiescent conditions are disturbed during the excavation of the scale and sludge. Clearly, the conventional ap-



1 Primary wash—removes additional oils and slimes
2 Secondary wash—solvent comprises water and detergent—removes oil traces
3 Tertiary wash—removes traces of solvent
4 Vacuum filters—operational and standby
5 Thickener underflow pumps—operational and standby
6 16" diameter return line—valves determine rate of return—5 hrs at 1500 GPM
7 6" blowdown line—valves determine flow rate—5 hrs at 1250 GPM—19 hrs at 1500 GPM
8 Return line from blowdown water treatment plant—25 GPM with 10% solids
9 Backwash rate—10 minutes at 5300 GPM—metered output from surge tank—1546 GPM
10 Sludges contain up to 50% solids by weight
11 Manifold with flow-adjusting valves
12 Waste chute—backup vacuum filters disconnected



proach to managing these sludges has not provided a satisfactory solution to the problem.

The new process

Colerapa Industries, Inc. (Ravenna, Ohio) converts a sludge that represents waste with serious handling and disposal problems and returns 95–98% of it as usable product having an iron content in excess of the best iron concentrate available. Typically, the material recovered from the process contains 72% total iron and negligible silica; today's best iron ore concentrates contain about 62% total iron with 8–12% silica. The recovered material is put back into a sinter plant or agglomerating facility, and hence right back into the iron-making process.

The Steel Company of Canada (Stelco) has been using the process at its Hilton Works Plant (Hamilton, Ontario) since September 1968. The processing services are provided by Euramca International Co. (Hamilton, Ontario). Recently, additional sludges previously wasted from other hot-rolling mill operations have also been trucked to the process station for processing and recovery.

Stelco superintendent of utilities and environmental matters T. Mair says, "the solids from the rolling operations is usually 3% of the 'put through' tonnage at the mill. It is a substantial volume of material that requires treatment. Although the particular Euramca installation is handling only a portion of the total solids being generated in the entire mill complex, we estimate that the volume of sludge handled is 40,000 tons per year and increasing as more of the mill becomes dependent on the sludge processing operation."

Mair adds, "Euramca International is under a 10-yr contract to provide similar sludge processing services in our new Nanticoke Plant which is due to start production in September 1977. The use of this system is in keeping with Stelco's utilization of the best practical technology in its continuing program of environmental quality control which to date has involved actual or committed expenditures in excess of $104 million."

The total capacity of the existing Hamilton Works plant is 6 million tons of steel per year. At the new plant in Nanticoke, Ontario, the steel production capacity is projected at 1.2 million in 1977 and goes up to 3.0 million tons by 1980.

How it got started

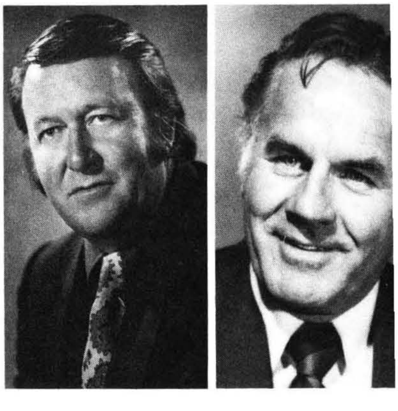
Inventor L. A. Duval of Aurora, Ohio, says that he started the Euramca operation with four people in 1968. Earlier, in 1963 under the Hess-von Bulow name, Duval did work for several steel companies in the U.S. including Republic Steel in Warren, Youngstown and Cleveland, Ohio; Sharon Steel in Farrell, Pa.; and U.S. Steel at McDonald, Ohio and Lorain, Ohio.

On the Republic Steel project in 1963, Duval tells how, within 90 days, he and associate J. R. Burton set up a mill sludge-processing plant. In this first practical application the project consisted of the excavation of the entire river bottom of the Mahoning River in the Youngstown and Warren area of Ohio. The river bottom contained years of accumulation of industrial wastes from chemical plants, municipal sewage treatment plants, leather processing plants, as well as steel plants. The problem of separating other than steel mill wastes had to be solved in order to process the steel mill oxides for reuse into the mill operation.

The sludge processing plant consisted of a new hydraulic dredging operation that lifted the solids and transported them to a floating mineral dressing plant that was attached as an integral part of the dredging unit. The dredge and process plant weighed 126 tons, was mobile, and floated on the river water.

The unit excavated and processed the river bottom concentrating the iron values that were pumped by pipeline to the shore while disposing of the tailings at the rear of the floating processing unit. Three units operated in the Mahoning River over a distance of 16 miles and salvaged 278,000 tons of finished concentrates from the bottom of the river. The average analysis of this material was 69% total iron with 3% silica.

In addition to efficient excavation at the pit, another important benefit of the Duval process is removal of oil contaminants from mill scale in order to prevent detrimental effects on the operation of pollution control systems at the consuming sinter plant. Air pollution problems at agglomerating facilities such as sinter or pelletizing plants has necessitated scrubbers or fabric filter collectors to alleviate this problem. These air cleaning methods are hampered by hydrocarbons transported as a coating on the particulates from the settling pits. Oils present with iron particulates cause condensation in the plant's air handling system, creating serious maintenance problems on the fans and ducts.



Stelco's Mair and Inventor Duval
converting sludge to better use

In the past, some steel mill operations have consumed these initial pit solids (the mill scale) in their sinter plant. However, with the required addition of air handling and pollution control facilities, the hydrocarbon carryover has caused maintenance and operation difficulties that dictate the most complete removal of oil from these solids, thereby limiting the use of this material that should be considered prime raw material.

Companies in the slag (the 22%) reprocessing business include Heckett Engineering Co. (Butler, Pa.); International Mill Services (Philadelphia, Pa.); and Edward M. Levy Co. (Detroit, Mich.).

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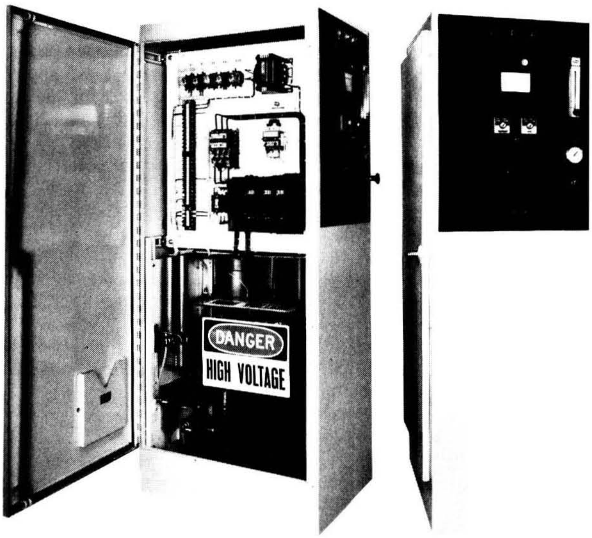

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FEATURE

Sodium scrubbing wastes

Insolubilization processes improve disposal options

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Sodium alkalis for scrubbing of flue gases to control SO_x emissions are better sorbents than calcium alkalis—lime or limestone. Yet, sodium alkalis, the compounds of choice in recycle systems, which are slightly less desirable in "throwaway" systems, have one major disadvantage: the "high" solubility of the end-product sodium sulfates and sulfites.

Industrial Resources, Inc. (IRI), a Chicago company, has developed methods to "insolubilize" sodium sulfate, both through an aqueous and a sintering process. The resultant compounds offer new methods of disposing of sulfates.

The impetus

IRI's interest in developing new sodium disposal techniques stems from the fact that the company holds federal leases for the mining of nahcolite (sodium) ore in western Colorado. This nahcolite ore assays 60–85% $NaHCO_3$, and can be used as an SO_x sorbent in scrubbing processes.

In discussions with utilities on the use of nahcolite ore as an SO_x sorbent, it appeared that the problem of sodium sulfate disposal could pose a worse problem than the SO_x emissions. Without a low-cost regeneration process, sodium as an SO_x sorbent was not attractive to utilities unless the solubility of resulting sodium sulfur oxide wastes could be reduced. Utilities did not want to substitute a water pollution problem for an air pollution problem.

To have an available sodium scrubbing process that competes as a throwaway process with lime or limestone wet scrubbing requires:

- a plentiful source of crude sodium at a reasonable cost
- a potentially approvable method of disposal of sodium sulfate wastes.

Raw nahcolite ore answers the first requirement. And IRI has 8,358 acres in western Colorado under federal lease on which there is an estimated resource of 100 million recoverable tons of nahcolite ore in the uppermost four beds of the deposits, and substantially more nahcolite is available if the remaining bedded and disseminated deposits are included. Because the raw ore is useful in a crushed or powdered form without need to further beneficiate, the cost does not include a premium for upgrading. A high quality product, such as glassmakers-grade soda ash, is really unnecessary for flue gas SO_x scrubbing. Raw ore in lump and powdered forms are shown in Figure 1.

To achieve the second requirement necessitated a 100-fold reduction in the solubility of sodium sulfates and sulfites from the 100–500 g/liter solubility level of these salts to the 2.3 g/liter level of calcium sulfate—the accepted industry standard. This reduction in solubility has been accomplished through research sponsored by IRI and conducted at Battelle Memorial Institute's Columbus (Ohio) Laboratories under the direction of Drs. Joseph M. Genco, Harvey S. Rosenberg, and Russell B. Bennett.

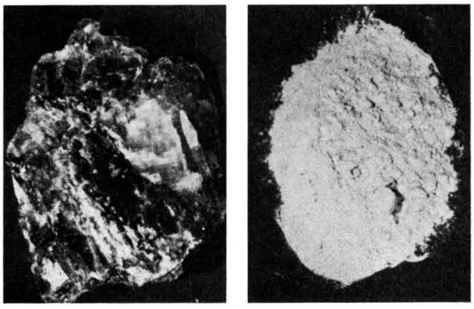
Aqueous insolubilization

One method for reducing the solubility of sodium sulfates/sulfites, primarily the idea of Edward C. Rosar and called the FERSONA process, involves the formation of relatively insoluble, granular crystalline precipitates; this is accomplished by reacting waste sodium sulfate with acidic ferric ion solutions to form double salts of sodium ferric hydroxy disulfates; as found in nature these species are known as sideronatrite and natrojarosite (Figure 2). The reaction conditions are relatively mild—atmospheric pressure and temperatures of 120–150°F. Unlike calcium sulfate/sulfite wates, the resulting precipitates do not form a thixotropic, water-retaining sludge, but may be easily dewatered to dryness. Solubilities of sideronatrite and natrojarosite (see table) are 10 to 100 times less than calcium sulfate; this is equivalent to a 10^3–10^4 reduction in the starting solubility of sodium sulfates/sulfites, and is well below the calcium sulfate standard.

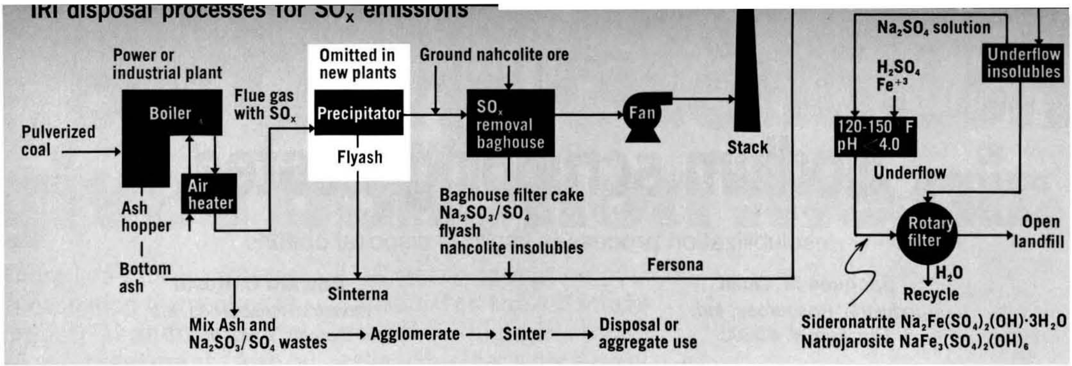
Continued research into this FERSONA process has extended its range of applicability. The process chemistry has successfully insolubilized sodium sulfate wastes from a variety of scrubbing processes, using both sodium carbonate and bicarbonate as the sorbent. Indeed, it appears that neither the source of the sodium, nor the means or manner in which the scrubbing process produces the sodium sulfate/sulfite is particularly critical.

Perhaps the most startling application is with nuclear power plant wastes. Nuclear plants may typically use cooling towers for heat dissipation by evaporation of water from natural sources. Such sources may contain about 15–250 ppm Na^+ and $SO_4^=$ ions, which are concentrated during the recirculation in the tower to about 10,000–50,000 ppm. This waste "magma" poses a serious disposal problem since it amounts to an estimated 15 tons per year/MW. IRI's FERSONA process technology has been applied to a waste typical of cooling tower magma to produce an insoluble precipitate. The technology can be applied to similar wastes from any cooling tower, whether associated with a nuclear or fossil fuel-fired plant. The FERSONA process is also a solution to the problem of disposal of sodium sulfate-containing wastes from demineralizers (for boiler feed water), an indispensible part of any power or industrial plant. These applications of the FERSONA process—disposal of cooling tower and demineralizer wastes—are the subject of U.S. patent 3,876,537 granted to IRI in April 1975.

FIGURE 1



IRI disposal processes for SO_x emissions



A hidden bonus of the FERSONA process is its applicability as a method of disposal of other wastes, such as waste crude sulfuric acid, steel pickling liquors, acid mine waters, and pyrites dump leach waters. These wastes typically contain sulfuric acid and/or sources of ferrous or ferric ion useful as FERSONA process technology.

Further, in some situations such as mine mouth power plants where there is a pyrites dump leachate or acid mine water problem, the sodium sulfate/sulfite wastes from sodium scrubbing of flue gases could be combined with the waste leach or mine water to dispose of both simultaneously.

The FERSONIUM process is the sister of the FERSONA process. As the name suggests, it deals with disposal of ammon*ium* sulfates and sulfites by aqueous reaction with acidic ferric solutions. The FERSONIUM process produces the analogous ammonium ferric hydroxydisulfates as granular precipitates, with a similar order of magnitude reduction in the solubility

SINTERNA process

Another approach pioneered by IRI for the disposal of sodium sulfate wastes from SO_x emissions control processes that use sodium alkali sorbents is its SINTERNA process. This process involves mixing the sodium sulfate wastes with powdered fly ash and/or bottom ash, pelletizing or briquetting the mixture, and sintering the briquette. A sintered briquette is shown in Figure 3.

The developmental work, also done at Battelle Columbus Laboratories principally under the direction of Dr. Russell Bennett, was concerned with simultaneously disposing of the sodium sulfate values while reducing the fly ash dusting problem. In accelerated leaching tests, pellets have shown sodium solubility to be reduced to about equal to or less than that of calcium sulfate. Again, this is a reduction of about two orders of magnitude in the solubility of the sodium salt.

The SINTERNA process is a method of disposal of wastes in a dry form, and the sintered briquettes show indications of having potential value as aggregate materials. Further, during the sintering, there is as high as 99% retention, that is, less than 1% of the sodium sulfate is lost as evolved SO_2 gas.

Calcium disadvantages

The implications of the IRI developments must be viewed from the background of penalties paid for the use of calcium alkali flue gas scrubbing. These penalties have been severe. Lime or limestone must be used in a wet system because of the relative inactivity in a dry system, except at unrealistically high temperatures. Wet systems require reheat of the flue gas after scrubbing. This reheat costs 2 to 5% of the total power plant energy output (not counting scrubber energy requirements). Scrubber internals tend to set up aerodynamic vibrations within the scrubber-stack systems. Chlorides in the water or coal tend to cause stress corrosion of stainless steel tubes.

In addition, there is the problem of scale formation inside lime or limestone scrubbers caused, in part, by the inverse solubility of calcium sulfate. Since the calcium source, lime or limestone, is a low solubility particulate, its presence in scrubber water adds to abrasion problems. The alternative is to increase the quantity of water, particularly where high quantities of fly ash are to be removed from the flue gas. This means greater water usage, which in the southwest may not be possible. It also means greater pumping costs and additional holding tanks and recycle lines to improve the utilization efficiency of the calcium within the scrubber. Single pass scrubbing becomes too inefficient at high dilution factors.

Finally, the calcium sulfate/sulfite sludge problem may be the penalty "straw that breaks the camel's back." Of course, the double alkali process is an attempt to use soluble sodium alkalis *inside* the scrubber to reduce the capital costs of the scrubber chamber itself and to improve reactivity while lowering the water requirements. However, the double alkali process merely moves the problem downstream since the external reaction with lime (and optionally, also, limestone) in turn produces the same calcium sulfate/sulfite sludge.

There are recent data to believe that calcium sulfate/sulfite sludge poses other disposal problems. Since the sludge is thixotropic, it cannot be piled above the ground and must be ponded. Typically, the ponds are constructed in clay formations. However, gypsum has been used for years to improve

FIGURE 2

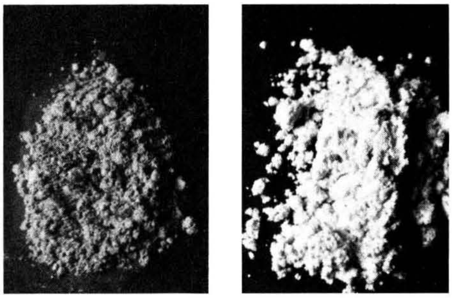
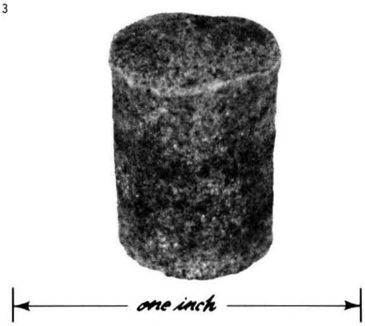


FIGURE 3



Relative Solubilities

Component	Solubility and conditions
Anhydrous Na_2SO_4	488 g/liter @ 40°C
Monoclinic columnar	
Rhombic (thenardite)	427 g/liter @ 100°C
	47.6 g/liter @ 0°C
$Na_2SO_4 \cdot 10H_2O$ (Glaubers salt)	110 g/liter @ 0°C
$Na_2SO_4 \cdot 7H_2O$	195 g/liter @ 0°C
$Na_2SO_3 \cdot 7H_2O$	328 g/liter @ 0°C
Na_2SO_3 anhydrous	125.4 g/liter @ 0°C
$CaSO_4 \cdot 2H_2O$ (Industry standard)	2.3 g/liter @ R.T.[a]
$CaSO_3 \cdot 2H_2O$	0.043 g/liter @ R.T.
$MgSO_4 \cdot 7H_2O$	710 g/liter
Sideronatrite	0.55 g/liter @ R.T.
Natrojarosite	0.37 g/liter @ R.T.
Ammoniojarosite	0.37 g/liter @ R.T.

[a] Room temperature

the permeability of clay. Thus, there is a potential that calcium sulfate sludges may act to increase the permeability of the clay formations underlying the ponds, permitting leaching of calcium sulfate/sulfite, magnesium sulfate, and heavy metals.

Sodium disposal methods

In contrast, sodium sulfate/sulfite wastes are not sludges and, thus, do not pose sludge-related handling problems. However, they do have a solubility problem. Ocean dumping is one method of disposal of sodium sulfate wastes; other methods include deep well disposal, isolation clay cell landfill and playa lake dumping in the western U.S. Playa dumping has been approved in California, and has been practiced by the Reid Gardner Station of the Nevada Power Co. in Clark County, Nev., for over one year with no adverse environmental effects. Reid Gardner is using once-through sodium scrubbing on two 125-MV units, and a scrubber for a third 125-MW unit is under construction. Since playa lakes contain very substantial quantities of sodium salts, including sulfates, sulfites, chlorides, and borates, return of those waste materials to the playas is considered essentially a conservation of the sodium salts, and does not significantly change the overall percentage of sodium sulfites or sulfates in the dry lake deposits.

To these current disposal methods should be added IRI's FERSONA and SINTERNA insolubilization processes. However, these latter processes may be more attractive since they are not site-specific, as are dumping, well disposal or landfilling.

The implications of dumping, landfilling, and well disposal, permanent disposal methods, are important. The nation in effect may have delayed the adoption of proven methods of sodium scrubbing by requiring the utilities to solve all the problems of disposal before doing any scrubbing. A better approach may be a more classical, two-generation development.

Throwaway scrubbing

In the first generation, utilities can concentrate on scrubbing, while practicing interim disposal of the scrubbing wastes. This gives pollution control or chemical industries time to develop second generation processes for recycle, regeneration or utilization of wastes. Typically, sodium regeneration costs more than scrubbing, and requiring the utilities to pay these costs now seems to be misplaced. Rather, the development of regeneration and the capital costs thereof are more appropriately the function of chemical companies. Chemical companies are better suited to the business of regional regeneration of SO_x sorbents for utilities or industrial plants, or processing of wastes to produce useful products.

Utilities could reduce their emissions control capital costs by using wet or dry sodium scrubbing followed by throwaway disposal or storage. The disposal of the wastes could be by ocean dumping, deep well disposal, playa lake dumping, isolation clay cell landfill, FERSONA or SINTERNA processing. These disposal methods represent first generation technology that IRI believes is available.

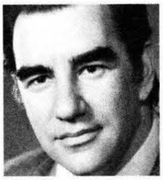
By way of example, a flow diagram shows a dry sodium scrubbing with nahcolite ore followed by IRI's FERSONA and/or SINTERNA disposal processes. The baghouse serves as a particulate collection device as well as a site for the nahcolite-SO_x reaction, while the nahcolite functions as a particulate filter aid and an SO_x sorbent. The dry reaction eliminates flue gas reheat, reduces process energy (water pumping) costs, and permits handling of dry wastes rather than sludges. Success of baghouse collection of fly ash under power plant conditions has been demonstrated at the Sunbury Station of Pennsylvania Power & Light (PP&L). These baghouses have been operating continuously at better than design specifications for two years. Typically, PP&L burns a mixture of petroleum coke (15–35%) and anthracite coal. PP&L's anthracite coal ash is 25%, the pressure drop through the bags is between 3–4 in. W.G. (design was 5 in. W.G.), and ash removal exceeds 99.5%. Apparently the bags have not been damaged by superheater tube leakage or temperature drop below dewpoint. After startup, maintenance has been less than design expectations. While these baghouses do not use nahcolite ore, the nahcolite ore baghouse injection process chemistry has been proven in full-sized bags.

Second generation technology would be the development of sorbent regeneration, or extractive processing of the sodium and/or sulfur values from the waste materials. This, it would appear, is the function of chemical, mineral supply or pollution control companies on whom would fall the burden of second generation capital investment. Their recycled product would then be returned to the utilities for reuse in the scrubber. For example, a single processing plant centrally located in Utah or Arizona could service the present or proposed 16 power plants of the southwest region.

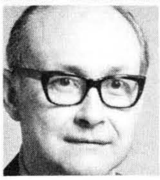
Current plans

IRI is currently working toward development of an estimated 100 million tons of its reserves of low-sulfur coal in the Book Cliffs coal field, along with related water rights on the Colorado River near Loma, Colorado. This is in addition to its work with nahcolite ore from the Piceance Creek Basin for SO_x emissions control and as a feedstock for soda ash production. IRI is a partner in a joint venture for copper and silver exploration in Oklahoma. IRI also holds claims on substantial reserves of chemical grade limestone, about 98% $CaCO_3$, in the Glenwood Canyon, Colorado area.

Within this context, IRI is carrying on its pollution control research in the utilization of nahcolite ore as an SO_x emissions control sorbent. IRI is reviewing potential commercial applications of the FERSONA, FERSONIUM and SINTERNA processes to sodium sulfite/sulfate wastes disposal. However, since IRI is not a pollution control hardware manufacturer or systems supplier, it also seeks further development of these processes through joint ventures, licensing, or sale of the technology.



Jacques M. Dulin *is president of Industrial Resources, Inc. He has a background in chemical research and development work, and has been in private practice as a patent attorney. Mr. Dulin is a co-author on a number of articles in the pollution control and legal fields.*



Edward C. Rosar *is vice president-exploration and mining operations of Industrial Resources, Inc. Mr. Rosar is a patentee and co-author of a number of papers in the mining and pollution control field. He formerly served in the U.S. Army Corps of Engineers.*

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GC in environmental analysis

Gas chromatography can be used to quantitate various gases, complex organic molecules, metals, anions and pesticides in the lab or in the field

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Chromatography is the most rapid and efficient technique for the separation of the components of any given system. It has been practiced for seven decades though it was not widely recognized until the forties. Gas phase chromatography, first developed in the fifties, has been applied to every aspect of analytical chemistry including application to the environment where it is currently being used for the analysis of the macro- to subpicogram quantities of various gases, complex organic molecules, pesticides and, more recently, some metals and anions. The number of organic compounds in the environment is very large, and it is in this area that a prima facie case exists for the use of gas chromatography either as a fingerprinting tool or as an integral part of the absolute identification of the species present.

If any one method of instrumental analysis is to come close to truly universal applicability, it will be gas phase chromatography. Not only is it nearly universal in applicability, but it is rapid, usually on the order of minutes per sample; it is extremely sensitive, it can detect subnanogram (10^{-9}) to subpicogram (10^{-12}) quantities; and it is capable of reliably being used in the field. It is not advocated that gas chromatography will become the universal method of analysis. Among many other analyses, acidity measurements will still require pH meters, alkali metals will best be determined by atomic absorption and ultra-trace analyses of metals will best be performed by neutron activation methods.

It is rare that any one technique, including gas chromatography (GC), can fully answer all aspects of an environmental problem. The researcher must make all attempts to remain aware of alternative methods that can compliment, though not necessarily replace, existing approaches to a problem.

Numerous research papers exist on the application of gas chromatography to the environment. It is beyond the scope of this article to comment on even a small percentage of them. An attempt will be made, however, to indicate some of the important advances and how they directly apply to environmental analysis, or to suggest where they will be of importance to environmental chemists in the near future.

Several recent articles of interest to environmental analysts appeared in the November 1973 issue of *J. Chromatogr. Sci.*, and another that suggested standard referee GC methods in atmospheric hydrocarbon analysis appeared in the February 1974 issue.

Hardware

Gas chromatographs are probably the best buys for any type of analytical equipment available today, particularly in view of their diverse applications. Basic systems, quite useful in many aspects of environmental analyses, are available for less than $1000; but, the usual price range is around $3000–8000, which could include a small dedicated computer system in the readout. Indeed it would be hard to exceed $11,000–12,000 total price for a complete gas chromatographic system, unless somewhat larger computers are needed as they are for the interpretation of complicated pyrolysis patterns, or if a mass spectrometer is needed as the detector-analyzer [*Environ. Sci. Technol.* **8,** 28 and 31 (1974)]. McNair and Chandler have published an article [*J. Chromatogr. Sci.*, Sept. 1973] dealing with available gas chromatographic equipment, and several other 1973 issues of that journal deal with supports and liquid materials (March and April) and detectors (May).

The detector is a critical component of any GC system, and it principally determines the limit of detectability for any given substance. Approximately two dozen different kinds of detectors are available for GC analysis [*Anal. Chem.* **43,** 113A (1971)]. Seven of the more common detectors are listed in Table 1, several of which are briefly discussed in this article.

Caution is advised when looking at the sensitivities of GC detectors. The published values, as here, are best detectabil-

TABLE 1

Gas chromatographic detectors

Detector	Detectability (g/sec)	Comments
Thermal conductivity	10^{-6a}	Despite the relatively low detectability of this system, it is probably the most widely used for virtually any kind of substance.
Flame ionization	10^{-12}	Nearly a universal detector; however, many gases of interest to environmentalists give little or no signal.
Alkali flame ionization	10^{-15}	Tremendous sensitivity for phosphorus compounds (pesticides). Otherwise, limited to compounds of nitrogen, sulfur, and halogens.
Flame photometric	10^{-12}	Limited application to phosphorus and sulfur compounds.
Electron capture	10^{-14}	Very useful despite its limited sensitivity to halogenated compounds and other electronegative atoms.
Helium ionization	10^{-14}	A universal detector, but "limited" to low temperatures (<100°C) and to the type of column used. Very sensitive to leaks and contamination.
Mass spectrometer	10^{-15}	Very expensive but essential to the absolute identification of components in many analyses. A universal detector.

[a] See text for comments on a device used to increase the detectability of this detector, and theoretically others, by three orders of magnitude.

ity values. Thus, the 10^{-14} g/sec value for the electron capture detector is valid only for some halogenated compounds; lightly halogenated substances are not particularly susceptible to detection by this device, and its performance is about five orders of magnitude poorer for compounds such as hydrocarbons. Moreover, since most detectors are fairly readily swamped with relatively small quantities of a liquid sample (more than 3 or 4 μl; capillary columns are swamped by much less) or more than 3–5 ml of a gas sample, the concentration in the sample must be relatively high compared to the detectability. For example, if a detector will respond to 10^{-12} g of a given substance injected in organic solution then, since only 2 or 3 μl can be injected, the concentration must be on the order of 10^{-9} g/ml (1 ppb).

Linear dynamic ranges of the detectors vary too. The electron capture detector is generally usable over about three orders of magnitude of concentrations (new models offer up to six orders of magnitude), whereas others, such as flame ionization, can be quantitatively utilized over six or seven orders of magnitude of concentrations. Therefore, despite the seemingly great detectability (<1 ppb) for GC systems, strong arguments for a lack of detectability can be made when environmental analytical needs are considered. Some naturally occurring compounds are active at or below the ppb level, thus analytical errors can enter in two ways—in the required concentrating steps, and if one operates the sensor near its limits of detection [*J. Chromatogr. Sci.* **12,** 36 (1974) and **12,** 80 (1974)].

Gas chromatography is being used in the field and laboratory for the quantitative analysis of:

- nearly all gases
- pesticide and PCB residues
- most smaller organic compounds
- more complex organic molecules such as alkaloids and steroids.

It is blossoming in the area of:

- some trace metal
- and anion analyses.

And should be applicable in a few years for:

- many other metals
- anions
- large organic molecules other than by pyrolysis.

Thermal conductivity

If the components of a system are concentrated enough, the simple thermal conductivity detector can be used. General analysis of auto and stack exhausts, or for fairly accurate analyses of oxygen, nitrogen, argon and carbon dioxide in aqueous systems [*Deep-Sea Res.* **20,** 291 (1973)] are routinely performed in the field and at sea with gas chromatographs equipped with this simple rugged detector. Carbon monoxide in a clean atmosphere has a concentration range near the limits of detection of this device, and some preconcentration steps may have to be employed. Other gaseous components of interest to environmental chemists such as PAN and oxides of sulfur and nitrogen are at the parts per billion level in the atmosphere and are totally undetected by the thermal conductivity detector. Normally it would be better to switch to a pulsed electron capture detector, which is quite sensitive to electronegative atoms, than go through a massive preconcentration step in order to use the thermal conductivity detector for these trace atmospheric components [*J. Chromatogr.* **79,** 322 (1973)].

A fairly recent development [*J. Chromatogr. Sci.* **8,** 452 (1970)] extends the detectability of the thermal conductivity cell by three orders of magnitude so that it now becomes competitive, in many cases, with flame ionization detectors. In essence, the device is an extremely efficient hydrogen pump (transducer) constructed of palladium and a 2.5 μl detector volume. Hydrogen is used as the initial carrier gas through the separatory column, and then it is rapidly pumped away from the column-separated components; only a small volume of nitrogen (or other gas) introduced between the column and transducer as the carrier at a reduced rate of flow is left. The concentrated (10 to 100-fold) components are then carried to the very small thermal conductivity cell to achieve the overall 1000-fold increase in sensitivity.

Surprisingly many substances, such as 1-hexene and furfural, quantitatively survive the contact with hot (200°C) palladium and hydrogen so that they can be subjected to and unchanged by the transducer process. This is mentioned because, even though the exact conditions are different, platinum or palladium, on various supports in short-heated precolumns with a hydrogen carrier, reduce and cleave all functional groups from complex organic compounds (many of which are not otherwise analyzable by GC) so that the carbon skeleton (as alkanes) can be ascertained. Even if the compound is reduced its retention index is not altered. Oxides of carbon, nitrogen and, with some loss in efficiency, compounds of sulfur all pass unaltered by the transducer [*J. Chromatogr. Sci.* **8,** 452 (1970)]. If all or most of these parameters are to be simultaneously monitored, the potential now exists for one instrument to handle the job.

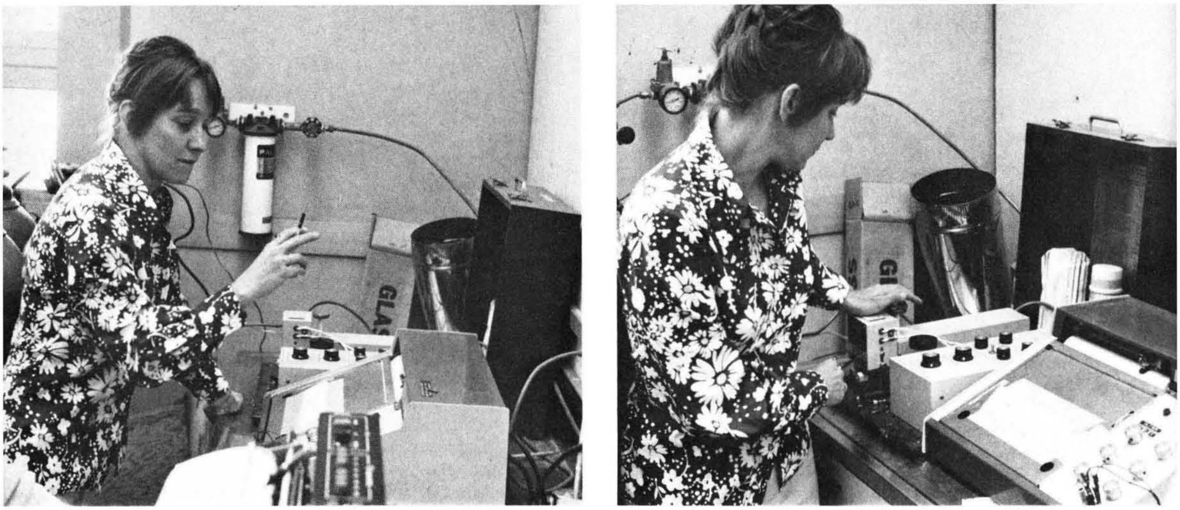
For routine air quality monitoring of gases such as CO and SO_2, continuous reading by infrared and flame photometric devices would be much more suitable than GC methods. But, individual case needs have to be evaluated in every instance. Only if the problem requires a knowledge of all the gases present does the use of a GC unit become mandatory.

Theoretically this in-system enrichment could be used for other concentration-dependent detectors (flame ionization, electron capture and, to a certain extend, helium ionization). However, there are other considerations, such as the flow rate, which are important for the full development of an instrument's sensitivity for detection of a given compound.

Other detectors

The helium ionization detector has turned out to be somewhat of a disappointment because of its extreme sensitivity to column bleed and leaks. These factors have earned it a reputation as being quantitatively unreliable when operated near its limit of detection. Nevertheless, since it is a universal detector, it is still very useful even when the sensitivity is throttled back by a factor of 100 or more, provided that the separation desired can be achieved on the limited selection of columns and at low temperatures (<100° C).

A recent development has been the modification of the electron capture detector so that it is operated as a gas phase microcoulometer with excellent detectability for certain molecules over a wide linear range of response [*Anal. Chem.* **43,** 1962 (1971)]. By using this method, Lovelock was able to follow air masses tagged with SF_6 at concentrations of parts



Gas chromatograph. *In the laboratory, the analyst injects a sample for plant metabolism studies*

per 10^{-12} by volume, and to make some interesting discoveries about iodine and sulfur. He found that enough methyl iodine (estimated at 40 million tons/yr) is released from the sea surface to account for half of the global iodine budget [*Nature* **241,** 194 (1973)]. Methyl iodide, it should be noted, is a potentially powerful methylating agent that could interact with other trace components of the atmosphere; however, because of its reactivity and short residence time in the atmosphere (estimated at 50 hr), it is probably hydrolyzed before significant quantities of it can interact as an alkylating agent. Based on these same GC studies of halogenated materials in the atmosphere, it is suspected, albeit unproven, that even carbon tetrachloride may be produced naturally in the atmosphere in quantities approaching anthropogenic production of one million tons per year.

As for sulfur, Lovelock notes that about 4% or 4 million tons of the annual sulfur budget crosses the sea interface into the atmosphere as dimethyl sulfide, there to be oxidized to dimethyl sulfoxide, sulfur dioxide and methanesulfonic acid that might be mistaken for inorganic sulfate unless specifically analyzed for by GC. It has also been demonstrated that soils moderately isolated from the atmosphere form dimethyl sulfide; hydrogen sulfide is not formed until the soils are completely isolated from atmospheric contact. The extent to which hydrogen sulfide formation occurs over land areas has not been evaluated, but it may turn out to be a significant portion of the sulfur budget; the extent of formation can only be successfully solved by gas chromatographic methods [*Nature* **243,** 181 (1974)].

Future developments

When the still-experimental hyperpressure (1000–3000 psi) gas chromatograph [*Rev. Anal. Chem.* **1,** 43 (1971)] becomes practical, hopefully in this decade, then the range of application of gas chromatography will be greatly extended. The essence of success of hyperpressure gas chromatography lies in the fact that when gases, which are about 1000 times less dense than liquids, are used at 1000 psi they begin to take on some of the solvent properties of liquids—they can cause the movement of otherwise nonvolatile substances through a gas chromatograph. Hyperpressure gas chromatography will facilitate the analysis of many large organic molecules, permit lower operating temperatures, lessen the need for derivatization before chromatographic analysis, and accept many more metal chelates that otherwise suffer thermal degradation, ligand exchange at elevated temperature or some other analytically undesirable trait.

Both anions and cations are now being reported as analyzable by gas chromatographic methods. Within the past few years approximately two dozen different anions of a dozen different elements (Table 2) have been reported as having been successfully analyzed by gas chromatography, some with sensitivity and accuracy to the 0.1 ppm level. For example, Butts and Rainey [*Anal. Chem.* **43** 538 (1971)] have reported the separation of the trimethylsilyl derivatives of phosphite, carbonate, oxalate, sulfate, vanadate, phosphate, and arsenate by using a temperature programmed GC equipped with a flame ionization detector. One of the essential differences between this method and the standard methods is that it is now potentially possible to determine these anions in a short period of time with only one common preparative procedure and one simultaneous analytical operation.

Of greater importance is the growing necessity to differentiate among the various possible species of any given element than to know its gross constituency in an environmental system. Only this differentiation will facilitate the comprehension of the mode of migration of the element, and it will be by GC methods, in many instances, that such discrimination will be effected. Interesting facets of sulfur and iodine migration were mentioned earlier. The input of those massive quantities of materials to the atmosphere is by microbial action, and it was through the use of gas chromatography that they were elucidated. We are now all aware, also via GC work, that nature supplies five times as much CO as man does to the atmosphere. Other GC work demonstrates that microbial action in the ocean alone allows for the passage of nearly 10^{14} g of nitrogen as N_2O to the atmosphere—equal to virtually all of the nitrogen flow into the oceans [*Nature* **247,** 181 (1974)].

Atmospheric trace metals

It is interesting to speculate on the other elements that are mobilized as gases by microbial action. In addition to sulfur, iodine, nitrogen, and carbon as the ubiquitous methane, at least four others—selenium, tellurium, mercury and arsenic—

TABLE 2

Anions that can be analyzed by gas chromatography

Arsenate
Arsenite
Borate
Bromide
Cacodylate
Carbonate
Chloride
Fluoride
Formate (probably)
Iodide
Nitrate
Oxalate
Phosphate
Phosphite
Silicates (various)
Sulfate
Vanadate

form stable volatile methyl compounds. It has been well over a century now since arsenic caused a stir in environmental health. Arsenicals were used in wallpaper paste to retard microbial spoilage; however, certain molds readily volatilize arsenic compounds to such a degree that a room can become quite toxic to humans exposed for a prolonged period to the room's atmosphere. Tens of millions of pounds of arsenicals in a variety of chemical forms are being used in the U.S. alone in pest control and for other purposes. Several methods are available to accurately analyze total arsenic present, but only the various forms of chromatography, including gas chromatography, can be readily applied to differentiate among the various chemical species of arsenic present in a system under study. In some cases, it may be the only way to distinguish between the quantity of a certain arsenic species being applied to a field or watershed against a background of other arsenical residues.

Since arsenic is known to be volatilized under suitable environmental conditions, some of the unanswered questions resolvable by methods that include GC are under what climatological and microbiological conditions is arsenic transported out of an arsenical-treated field or watershed by the wind, not as particulates, another important factor, but as a true gas, and how much?

Within the past decade environmental interest was generated when it became known that industrial losses of mercury were not harmlessly deposited in stream sediment beds, but were actively mobilized as stable methylated compounds up the food chain by microbial action. Even more recently, evidence has been produced to show that humic acids not only bind mercury ions, but also mobilize them by reduction to elemental mercury at free electron sites on the humic acids [*Science* **184,** 895 (1974)]. Quantitative GC methods have been devised for the determination of the various alkyl mercury salts [*Acta Chem. Scand.* **22,** 2277 (1968)], and inorganic mercury [*J. Chromatogr.* **89,** 201 (1974)].

Selenium, a trace element that is quite toxic at abnormally high concentrations, is actually a required element [*Science* **183,** 915 (1974)]. It too is known to form at least two volatile compounds in nature, and is easily lost in samples, presumably as a gas, unless special preservation steps are taken (storage in 1M HNO_3). Methods are available to quantitatively determine its concentration by colorimetry, fluorimetry, atomic absorption, neutron activation and by gas chromatography. Neutron activation is relatively slow, cannot be used in the field, and is applicable only when it is necessary to determine its presence at very low levels. Atomic absorption and fluorimetry are not readily amenable to use in the field; the former requires critical control during analysis and the latter, though offering slightly more sensitivity, is prone to interference problems, as is colorimetry. Thus we are left with gas chromatography as the reasonable choice for the determination of selenium down to the 0.1 ppm level without preconcentration measures. None of these methods will directly indicate the speciation of the selenium without considerable comparative wet chemistry, but only GC offers the greatest facility to determine how much is moving in the atmosphere as a gas and, since it is a field method, before any losses or changes can occur in storage.

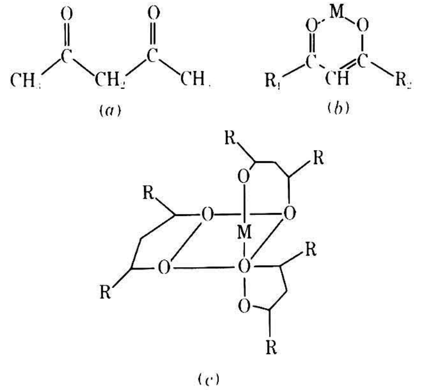
Given the ability to analyze for anions and other low-level gases by GC methods, there are two potential applications. First, if interferences make standard colorimetric methods difficult, an alternative technique with considerable resolution power now exists. Second, more detailed study of movements of the nutrients between the water-air interface is feasible.

Cation analysis

A convenient method for metal analysis by gas chromatographic methods has been sought for several decades. One of the early, successful methods was to convert the metals to halide salts. Such salts are sufficiently volatile for a number of metals to be determined in this manner. The drawbacks were that not all metals could be halogenated, high temperatures were required (≥300°C), traces of water caused hydrolysis problems, and the salts were corrosive to the apparatus.

Acetylacetonates occur naturally, and are suspected of being the transport agents for some metals in plants. Acetylacetone and various derivatives have been extensively used to preconcentrate metals, and to aid in the volatilization of these elements during their aspiration to the burner in flame and atomic absorption spectroscopy. Many metallo-organic complexes were tried in GC work, again with a mixture of success and failure. The principal drawback was that the complexes were not stable enough to tolerate the temperature (200–300°C) required to vaporize the sample. Recently, however, many of these same chelates have been tried again, but with one or more of the ligands containing a perfluoroalkyl group.

Acetylacetone and its derivatives



Acetylacetone (*a*); acetylacetonate of a univalent cation (*b*), and of a trivalent cation (*c*).

Perfluoroalkyl groups are desirable ligands to have on almost any substance to be analyzed by gas chromatography. They are inert, nonpolar groups and, thus, the volatility of the compound at elevated temperatures is significantly greater than the equivalent alkyl. This factor alone is most helpful to gas chromatography with a flame ionization detector, and to atomic absorption spectroscopy where thermal degradation of the compounds being analyzed had been a problem. Although many metal chelates, which previously decomposed at high temperatures, can now be analyzed by gas chromatography at lower temperatures (100–200°C), the perfluoroalkyl ligand has not proved to be the panacea. Most metals can now be detected at the parts per thousand level, but relatively few emerge quantitatively from the column at the parts per million or parts per billion level. Either the metal chelates are decomposing or are irreversibly absorbed on the columns at the lower concentration levels.

The future of GC metal analysis looks bright. Research in two areas should bring GC analysis of metals to complete fruition in this decade. One is to continue to study new ligand modifications, and the second is the complete development of hyperpressure GC, which has already been used to analyze 43 metal chelates at 115°C [*J. Chromatogr. Sci.* **8,** 25 (1970)]. Several acetylacetone derivatives incorporating perfluoroalkyl groups are commercially available, have been extensively tested, and are now being used to quantitatively analyze several metals by using GC.

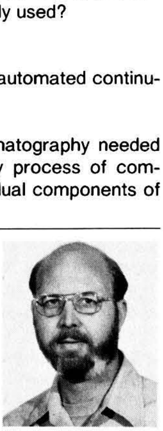
One of the more common chelating systems is "Htfa" where one R group is methyl and the other perfluoromethyl. The advantage of the perfluoroalkyl group in Htfa is that, for those metal chelates surviving the column conditions (Be, Al, Cr), detection down to the sub parts per billion level is possible because of the extreme sensitivity of the electron capture detector for polyhalogenated compounds [*Environ. Sci. Technol.* **6,** 155 (1972) and *Anal. Chem.* **47,** 165 (1975)]. The electron capture detector is actually detecting the perfluoralkyl groups, which were attached to the element in the preparation of the sample, rather than the element per se.

A second common chelating agent is referred to as "Hfod," where one R group is a perfluoropropyl and the other a *t*-butyl group. With the aid of this ligand, cobalt has been analyzed on a practical basis down to the 0.1 ppm level [*Gas Chromatogr.* 1970, p 369]. Alkali and alkaline earth metals, among many others, can also be analyzed by GC using Hfod, but the analysis is complicated by ligand exchange during chromatography. Symmetrical perfluoro systems—Hhfa where both R groups are perfluoromethyl—are too susceptible to hydration to be of much practical use. But, various synergistic reagents (dibutylsulfoxide or *i*-butyl amine) form stable adducts with the chelates of many metals in aqueous systems and have been analyzed at the parts per thousand level by using flame ionization detection. Thio derivatives of these Htfa and Hhfa systems seemed to be promising for a number of elements, including cadmium and lead [*Anal. Chem.* **43,** 2012 (1972)] but research in this area has lagged because of the instability of the ligand. Nickel and copper, among others, lend themselves to GC analyses by the use of various imino derivatives of Htfa [*J. Inorg. Nucl. Chem.* **35,** 1127 (1973)].

The question arises

If gas chromatography is such a good method of analysis, why isn't it used more frequently in environmental analyses? The answer to this question can only be found in the answers to other questions that the individual investigator must consider before each application. Among these questions the following general ones should be asked:

- Is GC or, for that matter, any other method under consideration for adoption, of equal or greater sensitivity and accuracy than whatever technique is presently used?
- Is GC any faster?
- What is the cost differential?
- Does the monitoring process require automated continuous readings?
- Does the project require field work?
- Are the separatory powers of chromatography needed either for fingerprinting or for the lengthy process of completely identifying some or all of the individual components of a sample?



Thomas A. Gosink *is a visiting associate professor at the Institute of Marine Science at the University of Alaska, Fairbanks. Dr. Gosink's research to develop trace metal analysis in aqueous systems by using gas chromatographic methods is funded under a National Science Foundation grant.*

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CURRENT RESEARCH

Problems of Measuring and Predicting Influence of Effluents on Marine Phytoplankton

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■ Concentrations of nitrogen (N) and phosphorus (P) in sewage effluents are high enough to increase the levels of these nutrients in coastal waters and thereby to influence phytoplankton ecology. A variety of algae cultured in several samples from one treatment plant failed to grow to the levels that would be predicted based on the N and P concentrations. Effluents from other treatment plants were even less predictable. Furthermore, different groups of algae and species within these groups varied in their response to different effluents which were matched in N and P concentrations. Effluent from one plant which produced deficient growth, based on the N and P concentrations, grew to expected levels when trace metals were added to the effluent. While N and P added to the coastal environment from sewage effluent stimulates general phytoplankton growth, the addition of effluents emphasizes the role of minor growth substances which might otherwise not have been important in the N-limited coastal region. These factors then become important in causing changes in the pattern of phytoplankton production, distribution, and population dynamics.

The input of municipal and industrial effluents to coastal waters has been and will continue to exert a major influence on the marine environment. In highly populated industrialized areas the concentrations of these substances can result in effects which may reach ecological proportions. Knowledge of the changes in the primary producers resulting from exposure to these pollutants is important in predicting the effects of pollutants on the organic cycle of the sea. Treated sewage effluents are a major portion of the volume of materials discharged to the sea and associated high concentrations of nitrogen and phosphorus most certainly affect the growth of marine plants.

It would be useful if we could predict by simple measurements of nitrogen and phosphorus in an effluent, the influence of sewage on the production, seasonal patterns, and populations of coastal microalgae. Experiments are described below in which the growth response of a number of cultured marine phytoplankton species were compared in treated sewage effluents from a variety of treatment plants in New England. Concentrations of the inorganic N and P in the effluents were used as the basis for this comparison.

Materials and Methods

Chlorinated sewage effluent was collected directly from the outfall of several New England secondary treatment plants and frozen in polycarbonate bottles. Cultures of phytoplankton were from the Woods Hole Oceanographic Institution Collection of R. R. L. Guillard and standard methods were used for experimentation—125-ml flasks, 12-hr light-dark cycle under cool white fluorescent lights (approx. 400 μW/cm^2 380–700 nm) at 20°C. Sterile techniques were employed up to the point of addition of sewage; the only treatment to the effluent was having been frozen. Controls for the experiments were grown in a modification of "f" medium (*1*) in which ammonium was substituted for nitrate and phosphate was doubled. Silicate, vitamins, and trace metals remained unchanged (*2*). The modified "f" medium was diluted so that the nitrogen level matched that in the seawater–sewage mixture (at a level of 100 μg-at. N per liter, the medium contained 100 μg-at./l. N, 8 μg-at./l. P, 6 μg-at./l. Si, 1.3 μg-at./l. Fe, 0.004 μg-at./l. Cu, 0.009 μg-at./l. Zn, 0.006 μg-at./l. Co, 0.1 μg-at./l. Mn, 0.003 μg-at./l. Mo and 0.49 mg/l. Na_2-EDTA$^+$, 0.011 mg/l. thiamine, 0.057 μg/l. biotin, 0.057 μg/l. B_{12}). Analytical methods used were: ammonia (*3*); nitrate (*4*); nitrite (*5*); phosphorus (*6*); silicon (*7*); iron, copper, zinc, and nickel by atomic absorption spectrophotometer (Jarrell-Ash Model 800 double-beam dual-channel). Relative growth was measured daily by in vivo chlorophyll measurements with a Turner fluorometer (*8*). Data are reported as a percentage of in vivo measurement of the experimental flasks compared to the control, at the end of the control's log growth phase. While certain batches of sewage increased the time required to reach log phase, this was never more than one day. Thus the comparative in vivo reading at the close of the control's log phase of growth represents an integrated value of yield, growth rate, and lag. Experimental growth flasks were run in replicate, in vivo chlorophyll was read daily, and growth curves were constructed from this information. Differences of ±15% from the control are significant at the 95% level of confidence.

Results

Inorganic Nutrients in Sewage Effluent. Ideally the secondary treatment of sewage results in the conversion of organic nitrogen and phosphorus to inorganic forms readily

Table I. Inorganic Plant Nutrients in Secondary Treated Sewage Effluents

	µg-at./LITER					
	NH_4	NO_2	NO_3	PO_4	Si	N:P ratio
Cranston, R. I.	1832	3	13	166	161	11.1
Warwick, R. I.	1791	4	48	304	136	6.1
Otis Air Force Base, Mass.	1769	8	16	233	165	7.7
Sanford, Me.	616	1	2	65	106	9.5
Olgonquoit, Me.	3	1	564	68	172	8.4
Plymouth, Mass.	205	2	182	124	116	3.1

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Table II. Changes in Inorganic Nitrogen in Nondiluted Cranston Sewage Effluent at Room Temperature

Numbers in parentheses are percents of total inorganic nitrogen remaining after one month

	Total inorganic nitrogen, %								
		Aerated				Anaerobic			
	Original sample	Chlorinated (21.5)		Nonchlorinated (37.2)		Chlorinated (103)		Nonchlorinated (66.5)	
NH_4	99	94[a]	3.4[b]	1	3.4	99	85.5	1	3.4
NO_2	0.4	5.9	84.5	99	0.1	0.6	13.0	99	0.1
NO_3	0.6	0.1	15.0	0.1	96.5	0.4	1.5	0.1	96.5

[a] After 1 week. [b] After 1 month.

Table III. Growth of Pure Cultures of Marine Microalgae in Cranston, R. I., Secondary Treated Sewage Relative to Growth in Complete Marine Medium as Control (Equal to 100)

All were matched in nitrogen and phosphorus.[a] Daily measurements of in vivo chlorophyll fluorescence were made; numbers represent the mean of three culture flasks at the end of log growth

	% Growth relative to medium control (100)	
	Sample A	Sample B
Diatoms		
Phaeodactylum tricornutum	165	87
Skeletonema costatum	93	48
Chaetoceros lorenzianus	110	42
Cylindrotheca closterium	100	44
Thalassiosira pseudonana (*C. nana* 3H)	134	74
Thalassiosira pseudonana (*C. nana* 13-1)	109	0
Coccolithophores		
Coccolithus huxleyi	210	119
Cricosphaera carterae	120	49
Dinoflagellates		
Amphidinium carteri	105	101
Exuviella sp.	119	120
Green microalgae		
Dunaliella tertiolecta	135	99
Nannochloris sp.	125	197
Stichococcus sp.	137	226
Chlamydomonas sp.	160	88
Chrysophyceans		
Isochrysis galbana	150	100

[a] Nitrogen = 100 μg-at./l; phosphorus = 8 μg-at./l.

Table IV. Growth of Pure Cultures of Marine Microalgae in Secondary Treated Sewage from Four Different Plants Relative to Growth in Complete Marine Medium as Control (Equal to 100)

All were matched in nitrogen (100 μg-at./l.)

	% Growth relative to medium control (100)			
	Cranston, R. I.	Otis AFB, Mass.	Warwick, R. I.	Olgonquoit, Me.
Skeletonema costatum	59[a]	83[b]	75	63
Thalassiosira pseudonana (*C. nana* 3H)	83	125[b]	52	44[a]
Coccolithus huxleyi	127[b]	10[a]	109	87
Amphidinium carteri	130[b]	107	118	34[a]
Exuviella sp.	120	0[a]	89	122[b]
Dunaliella tertiolecta	145	112	105[a]	235[b]
Nannochloris sp.	198	79[a]	125	106
Isochrysis galbana	111	93	121[b]	39[a]

[a] Poorest growth for species. [b] Best growth for species.

available for plant uptake (Table I). Generally little of the organic N and P is refractory and most leaves the treatment plant in solution as ammonium or orthophosphate. Depending on the type of operation, some effluents may contain primarily nitrate or mixture of nitrate and ammonia as samples from Olgonquoit, Me., and Plymouth, Mass., show (Table I). While the samples used in this work were taken directly from the chlorinated effluent discharge outlet and immediately frozen, it must be remembered that chemical and bacterial activity are continually changing the chemical nature of effluents in the natural environment. An example of such changes is shown in Table II. The data are not intended to show what occurs when effluent enters an estuary but only to indicate possible changes caused by oxidation and denitrification.

Phytoplankton Response to Effluents. If two samples of effluent are taken from the same secondary treatment plant a week apart, one would expect the absolute concentrations of N and P to be different. If the concentration of N and P are matched, however, we might expect the growth response of phytoplankton to be similar. This was not the case (Table III), but rather it is evident that the presence (or absence) of other substances in effluent are effective in regulating growth. In fact, some samples (Table III, sample A) resulted in more rapid growth than that obtained in complete marine medium. In the 18 samples assayed from the Cranston plant, phytoplankton grew better half the time; on one occasion the effluent was toxic.

Reduced growth in diatoms and coccolithophores was fairly consistent in sample B compared with sample A (40–50%). Dinoflagellates grew equally well in both samples while the green algae as a group responded erratically. *Nannochloris* and *Stichococcus* grew better in sample B differing greatly from the diatom and dinoflagellate group while *Dunaliella* and *Chlamydomonas* responded the same as diatoms and coccolithophores.

These data (Table III) show two important points: (1) The growth response of marine phytoplankton in sewage effluent even from the same treatment plant cannot be predicted from measurements of inorganic nitrogen and phosphorus alone; (2) the response of different phylogenetic groups and species within groups is different although the N and P concentrations in two batches may be the same.

Considering the variability found in effluent from one plant, it was not surprising that effluents (matched in inorganic nitrogen) from four different plants resulted in widely differing algal growth (Table IV). Note that all four batches of sewage stimulated best growth in some species and poorest growth in others.

Heavy Metals in Sewage Effluents. Heavy metals are important biologically as micronutrients, but at high levels may become toxic; they are also important constituents of municipal and industrial effluents. Measurements of a limited number of metals (Table V) indicate that effluents from different areas have distinctively different concentrations of metals. Cranston, R.I., is particularly high in nickel, reflecting the jewelry and metal finishing industries in that city. For unknown reasons, effluent from Otis AFB is high in copper and iron while Cranston, Plymouth, and Falmouth, Me., are high in zinc. These data serve to point out the complexity and variability involved in equating the influence of metals in different effluents. While one of the factors causing the various algal growth responses (Table IV) may be the high nickel concentration in Cranston sewage or the levels of iron and copper in the Otis samples, we were not able to determine any relationships in our experiments. Furthermore, synergistic effects and the fact that trace metals can be both stimulatory and inhibitory complicate the results. Patrick (*9*), for example, showed that

Table V. Metal Concentrations in Sewage Effluent from Seven Treatment Plants and Sludge from the Cranston, R. I., plant

	µg/l			
	Fe	Cu	Zn	Ni
Cranston, R. I.	214 (100–500)	53 (30–90)	159 (50–440)	358 (100–1120)
Warwick, R. I.	270	30	66	40
Plymouth, Mass.	200	10	140	40
Otis AFB, Mass.	960	300	70	40
Olgonquoit, Me.	300	10	60	40
Sanford, Me.	500	10	30	40
Falmouth, Me.	100	10	110	40
	µg/g dry wt			
Cranston, R. I. sludge	26,903	3346	8402	1465

Table VI. Growth of Marine Phytoplankton in Cultures with Dried Sludge and New York Bight Sediment Added Compared to Medium Control (100).

	Cranston, R. I., sludge[a]	N. Y. bight sediment[b]
Skeletonema costatum	0	0
Thalassiosira pseudonana (*Cyclotella nana* 3H)	0	65
Coccolithus huxleyi	0	0
Amphidinium carteri	0	54
Dunaliella tertiolecta	40	49
Nannochloris sp.	6	9

[a] 3.69 mg dry wt/50 ml culture. [b] 31.78 mg dry wt/ml culture.

high levels of manganese inhibit growth of blue-green algae more than green algae or diatoms. However, the toxicity of manganese to blue-green algae varies with the concentration of iron (*10*).

Another approach to assessing the effects of sewage on growth is to add factors to samples which had previously produced "deficient" algal growth. It is shown clearly that the effluent from Cranston was deficient in required trace metals (Figure 1). Additions of "f" medium trace metal mix resulted in growth equivalent to that obtained in complete medium "f" (Figure 1). Most of the metals were removed with sludge (Table V) which can be toxic to phytoplankton (Table VI). Two green algae *Dunaliella tertiolecta* and *Nannochloris* sp. were able to survive in cultures with sludge added (Table VI). *Nannochloris* was originally isolated from a polluted area in L.I. Sound (*11*). *Dunaliella*, a tide pool organism, has been shown to be tolerant to a variety of pollutants. Menzel (*12*) reported *Dunaliella* was highly resistant to chlorinated hydrocarbons, while Dunstan (*13*) showed that this species was also highly tolerant of the low-molecular-weight hydrocarbons in oil.

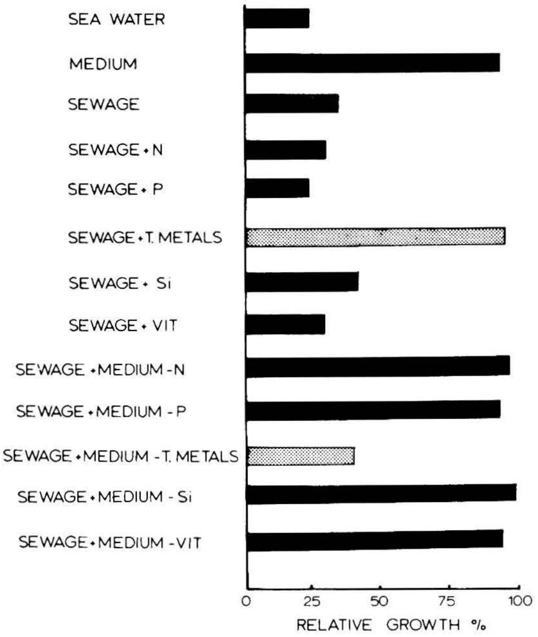

Figure 1. *Skeletonema costatum* growth in a "deficient" batch of sewage

Discussion

While it is tempting to use N and P to predict and model ecological changes caused by increased sewage effluents in coastal waters, evidence presented here indicates that such an approach must be used with caution. The general response of a rich nearshore community to effluent is one of enhanced growth of the total population as shown by C^{14} production (*14*) and continuous cultures studies (*15*). However, long-term effects result in a more subtle selection of species determined by species specific physiological requirements.

Since all phytoplankton use and require N and P, growth of all species is enhanced by sewage up to the point where other substances either in the sewage or occurring naturally in the seawater become limiting. Thus, the addition of sewage to the sea may actually cause limitation and/or species selection by trace factors like metals, chelation potential, organic load, and vitamins. These trace substances might otherwise not be important since most natural coastal areas are N limited (*16*). In freshwater environments, Morton and Lee (*17*) demonstrated the importance of iron in shifting population dominance from unobjectionable green algae to blue-green algae. The shift in dominance can occur without necessarily changing the algal biomass (*17*).

We have not considered in this study the toxic aspects of effluents (such as chlorine complexes, metals, and hydrocarbons) that will certainly be important in areas near outfalls. The lack of growth of some species represents an inhibitory response (e.g., Table IV, Otis AF Base, Mass., with *Coccolithus huxleyi* and *Exuviella* sp.) and certain batches of sewage in other experiments have been shown to be toxic (*2*).

The most significant force exerted by sewage discharge into the sea is to change the pattern of phytoplankton production, distribution, and population dynamics. The addition of or lack of minor growth factors, which are differentially required by phytoplankton species, controls the net result.

Furthermore, the results reported here using 15 organisms representing five phylogenetic groups, underscore the principle that a wide range of responses must be expected from the different physiological and ecological types composing the marine phytoplankton. In light of this, the ecological interpretation of results based on cultures of one or two species can be misleading. This is particularly important in studies of the ecological effects of specific pollutants (*12*) as well as toxicity bioassays and monitoring programs (*18–20*).

Acknowledgment

The author gratefully acknowledges the technical assistance of Helen Stanley and thanks David Menzel for critically reviewing the manuscript.

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Received for review August 12, 1974. Accepted January 14, 1975. Work supported by National Science Foundation Grant GT-32140 at Woods Hole Oceanographic Institution.

Trees as Environmental Sensors Monitoring Long-Term Heavy Metal Contamination of Spokane River, Idaho

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■ Ponderosa pine trees growing on the bank of the Spokane River, Idaho, have been used to monitor the river's past concentrations of Hg, Cr, Ag, Rb, Zn, Co, and Fe. Sections of cores and tree rings were neutron-activated to determine the trees' metal content as a function of tree ring age. Analysis of these data indicates that they are in rough agreement with sediment core data for Coeur d'Alene Lake and the volume of ore mined in the Coeur d'Alene mining district if allowances are made for metal holdup in Coeur d'Alene Lake.

Trees can be considered sensors that record the environmental disturbances. Climatic history is recorded in the tree rings (*1*). Variations in the radiocarbon content of the bristlecone pine (*2*) and the sequoia redwood (*3*) can be related to variations of the production of ^{14}C in the upper atmosphere (*4*), and fossil fuel burning (*5*).

Warren and co-investigators (*6–8*) have shown that leaves and so forth taken from trees grown in the vicinity of ore deposits contain orders of magnitude more As, Cu, and Zn than those grown in less mineralized areas and have demonstrated that Douglas fir concentrates As by a factor of between 10–100 greater than most other trees and plants. These observations demonstrate that trees are sensitive indicators of dissolved metal ion concentrations in soils. Ellis (*9*) determined the mineral content of the Grand fir [*Abies grandis* (Dougl.) Lindl.] grown east and west of the Cascade Mountains and observed higher Mo, Zn, Ag, Pb, and Sr concentrations in the eastern trees. Ellis (*9*) also reported significant differences in Cu, Zn, Pb, and Ag concentrations for trees grown in several drainage areas of the highly mineralized area of northeastern Washington and northern Idaho and observed that trees growing near salt water had abnormally high Na concentrations. Galligan et al. (*10*) observed variations of Mn concentrations in Douglas fir cores as a function of growth-ring age. Zinke (*11*) examined the trace metal content of a 2000-year-old redwood and found that the Zn content varied from 2.2–5.8 ppm with a period of about 30–50 years. Others (*12, 13*) have determined the Pb concentration as a function of growth-ring age for several tree species. Holtzman (*13*), who determined the ^{210}Pb content in black oak, white oak, and hickory, demonstrated that the ^{210}Pb concentration decreased exponentially as a function of growth-ring age. Holtzman's data (*13*) suggest that translocation, while not zero, is small enough that variations of Pb concentrations may reflect environmental factors. Data supporting the idea that metal ions are incorporated into growth rings via leaves and needles do not exist; thus, air pollution as a direct path for the introduction of metals into growth rings is unlikely. The research mentioned above shows that significant variations in the trace element concentration of metal ions in growth rings of trees have been determined and that they may be determined by environmental factors, and suggests the possibility of monitoring long-term heavy metal concentrations in streams by determining the heavy metal content of growth rings of trees growing on river banks.

Rivers flowing through the active Coeur d'Alene mining region of northern Idaho provide a good test of the above hypothesis because mining and smelting effluents discharged near Kellogg, Idaho, have polluted the Coeur d'Alene River, which drains into Coeur d'Alene Lake, the source of the Spokane River. Figure 1 is a map of the Coeur d'Alene region. Mining activity for this region is well documented (*14*). Furthermore, water quality parameters of the Spokane River and Coeur d'Alene Lake have been

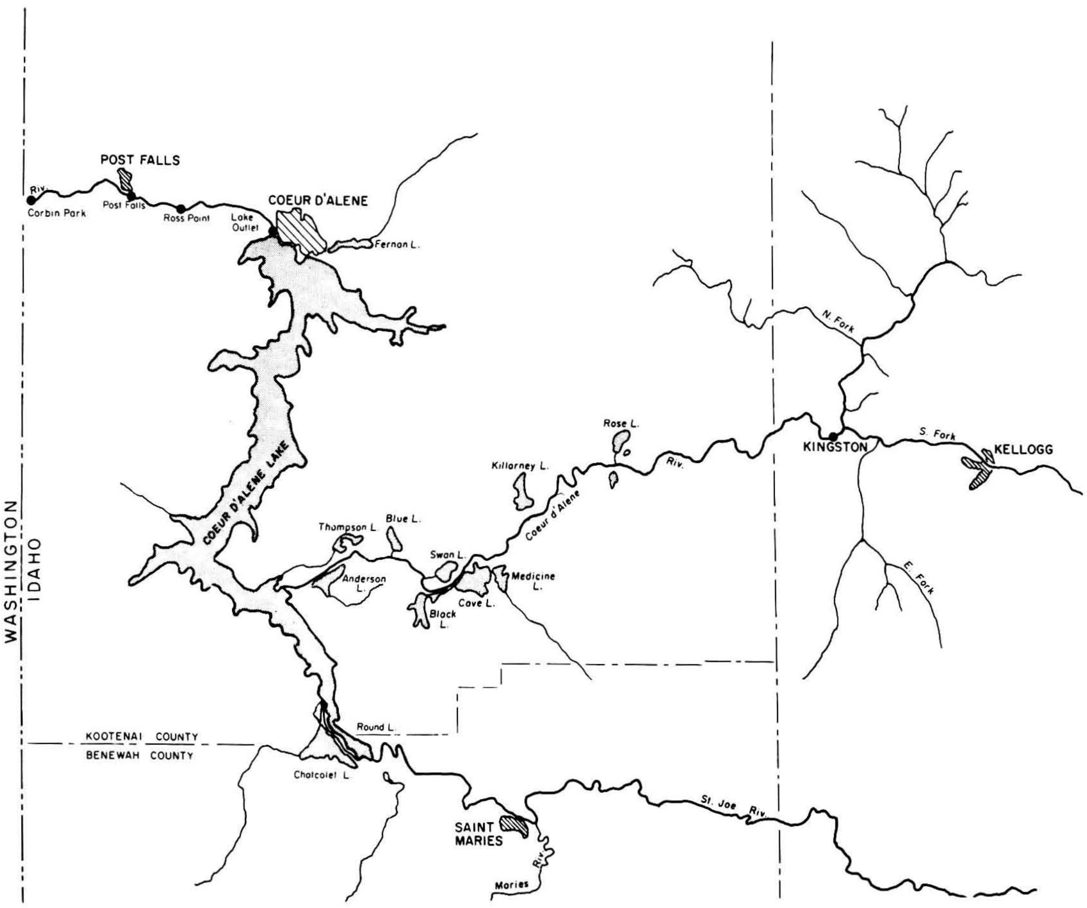

Figure 1. A map of the Coeur d'Alene mining region. Mining and smelting activities are near Kellogg, Idaho. The trees used in this study grew in the vicinity of Post Falls, Idaho, and were separated from the mining and smelting by a distance of 66 km and a mountain range

objects of intensive research (*15*). Of particular importance is the fact that Funk and Filby (*15*) determined the metals distribution as a function of sediment depth for Coeur d'Alene Lake. The sediment and mining activity data provide comparative bases to establish if the metal content in rings of trees growing along polluted streams can be used to record these water quality data for long periods of time. This is a report of an attempt to use three ponderosa pine trees growing on the banks of the Spokane River as sensors of the river's metal ion concentrations for the past 60–70 years.

Experimental

Cores were taken from ponderosa pine trees (pinus ponderosa) growing on the banks of the Spokane River at Post Falls and Ross Point, Idaho, to determine if metal concentrations in the tree rings of these trees varied significantly. These trees are separated by about 3 km and are about 66 km from the mining activity. The Post Falls ponderosa pine was a healthy 41-year-old tree growing about three meters from the high-water level of the Spokane River. The Ross Point ponderosa pine was growing on the bank edge (high-water level), was dying, and was older than 64 years. Since the cores from these trees were perpendicular to the tree rings, the concentrations for each section of the cores are averages for the rings (years) sampled, thus these data represent the results of a coarse-grained and preliminary attempt to determine if trees can sense variations of metal ion concentrations in the Spokane River. Individual growth rings of these trees could not be used because sample sizes would be too small for the precise determination of their metal content. A third ponderosa pine, about 57 years old, growing at Corbin Park, and with a large root in the Spokane River, was cut down and a section removed for analysis. Corbin Park is on the Idaho-Washington border and is about 12 km downstream from Post Falls. To obtain more refined data, cores parallel to the tree rings were taken from the Corbin Park tree at five-ring intervals. The Corbin Park tree is considered a "better" sensor than the Post Falls and Ross Point trees because of the larger samples used, considerably better counting statistics, the shorter time intervals sampled by the parallel cores and, most importantly, the fact that this tree had a large root in direct contact with the Spokane River.

The cores were dried to constant weight, divided into sections of approximately equal weight and neutron activated (along with Zn and Co standards) in the Washington State University Triga reactor. Copper flux monitors were included with each sample to correct for small flux differences.

Ge(Li) detectors were used to detect the gamma-emitting radionuclides present and the counting data were recorded with multichannel analyzers. Elemental concentrations (μg/g) in each section were calculated relative to Zn standards. Concentrations of other elements were calculated relative to the Zn data using gamma and isotopic abundances and half-lives found in "The Table of Isotopes" (*16*). Data for the Post Falls and Ross Point trees were combined to give the metal ion concentrations of these trees for the past 64 years, averaged over 6- to 10-year intervals. This was done because the outer Ross Point core, which comprised the dying portion of the tree, covered a 40-year interval—between 1931 and 1972—and did not yield information about fluctuations of metal concentrations. The average metal concentrations in the two trees were in reasonable agreement (±30%), but the Fe and Zn concentrations in the Ross Point tree were 3–5 times higher than in the Post Falls tree. The fact that Fe and Zn concentrations are quite different cannot be readily explained and serves to emphasize the fact that soil conditions, the tree's health, contact with the river and possibly other factors may influence metal uptake by the tree.

Silver, Zn, Co, and Fe were observed in all three trees, but only the Corbin Park data are included in Table I for the reasons mentioned above. The Na, K, Mn, La, Sb, and Au data from the Ross Point and Post Falls trees are included mainly to give an idea of their metal ion concentrations and for comparison to other data (*9*). Sodium, K, Mn, La, Sb, and Au were not observed in the Corbin Park tree because samples were counted after decay times sufficient to allow the short-lived radionuclides of these elements to decay away. This was done because Zn, Co, and Fe were considered to be better indicators of stream pollution and because of the high concentration (~400 μg/cc) of Zn observed in the Spokane River. Mercury and Rb were observed in the Corbin Park tree because of the longer irradiation and counting times.

Results and Discussion

Table I contains the metal concentrations found in the growth rings of the Post Falls, Ross Point, and Corbin Park trees. Examination of these data indicate metal concentration fluctuations, some significant at the 95% confidence level. To determine if these fluctuations could be related to environmental disturbances in the Coeur d'Alene mining district near Wallace and Kellogg, Idaho, the data were compared to the annual ore production (*14*). Examination of the mining data, shown in Figure 2, revealed maxima at 1918, 1928, and 1948 and minima at 1922, 1932, and 1954–57. The 1922 and 1932 dates represent economic depressions.

The Coeur d'Alene Lake sediment core data, previously obtained by Funk and Filby (*15*), were also compared to the tree ring data. The sediment core used for this comparison was taken 1.6 km from the mouth of the Coeur d'Alene River and was chosen because the sediment would be minimally disturbed by river scouring action. Sediment core data represent an even more coarse-grained approach to the detection of metal ion concentrations in the Coeur d'Alene River, but the problem of holdup in Coeur d'Alene Lake is eliminated. The sediment, tree-ring, and mining data are shown in Figure 2.

The Fe data for the Corbin Park and Post Falls trees showed one prominent, recent maximum. If these data are displaced about 15 years, they are in agreement with the one major peak observed at a sediment depth of 20 cm and the post-World War II mining activity maximum. It should be noted that the Fe concentration for the 1962–72 period of the Post Falls tree was 63.7 μg/g, compared to the peak value of 52.2 μg/g for the Corbin Park tree. Both the tree and sediment data indicate a major Fe peak reflecting the mining activity shortly after World War II.

When the Cr data for the Corbin Park tree are displaced about nine years, they are in rough agreement with the mining activity and the Coeur d'Alene sediment core data. The sediment core data lag the mining two to three years for the 1948 and 1928 mining activity peaks, but the 1917 mining peak follows the core peak by about five years.

On the basis of the $2.0\sqrt{2\sigma_{av}}$ criterion, it is difficult to correlate the Co data with the mining or sediment core data. There is a minimum that corresponds to the 1944–51 period and it is possibly related to the 1932–40 depression.

With the exception of the 1953–55 minimum, the Zn data for the Corbin Park tree correlate with mining activity. The Zn concentration in the Corbin Park tree decreases at about the same rate as the sediment but with a five- to ten-year delay. The recent decrease in Zn concentration in the tree and sediment may be indicative of more efficient Zn recoveries and decreased production at the upstream mines and smelters.

Table I. Metal Concentrations in μg/g of Dry Wood for Ponderosa Pine Trees Growing on the Banks of the Spokane River, Idaho

Date rings formed	Ross Point						Corbin Park						
	Na	K	Mn	La	Sb	Au	Hg	Cr	Ag	Rb	Zn	Co	Fe
1908–14	31.3	652	1.55	0.0044	0.0049	0.0017	...	...	...	...	...	...	...
1916–18	32.0	676	1.54	0.0053	...	0.0010	0.010	0.10	<0.02	0.17	100.2	0.067	16.5
1918–21							0.011	0.10	0.09	0.21	92.6	0.053	14.8
1925–27	108.8	631	1.21	0.0147	0.0029	0.0011	0.005	0.90	0.14	0.08	73.3	0.049	12.3
1930–32							0.010	0.10	0.22	0.06	107.2	0.051	14.0
				Post Falls									
1935–36	36.0	1381	1.32	0.0029	0.0023	0.0013	<0.007	0.58	0.12	0.73	90.2	0.064	17.2
1939–41	116.8	1588	0.97	0.0082	0.0028	0.0024	<0.007	0.15	0.06	0.48	109.3	0.046	11.3
1944–46							0.017	0.09	0.15	0.77	97.3	0.019	5.2
1949–51	117.0	3311	1.63	0.0015	0.011	0.0031	0.019	0.09	0.15	0.92	86.2	0.026	11.3
1954–56	71.0	3034	1.41	0.0049	0.0024	0.0011	0.019	0.36	0.09	0.67	78.3	0.050	10.7
1958–61							0.020	0.09	0.18	0.69	62.2	0.033	8.5
1965–66	143	2837	1.55	0.0051	0.0051	0.0035	0.016	0.14	0.09	0.80	41.0	0.026	52.2
1967–71							0.022	0.10	0.05	0.47	37.7	0.030	7.0
	0.5	39	0.04	0.0005	0.0002	0.0002	0.003	0.02	0.01	0.08	0.4	0.007	0.5[a]
	1.4	110	0.11	0.0014	0.0006	0.0006	0.009	0.06	0.03	0.23	1.1	0.019	1.4[b]

[a] These are the average standard deviations for each metal concentration, based only on counting data. [b] A significant difference is defined as $[C(1) - C(2)] \geq 2.0\sqrt{2}\,\sigma_{av}$.

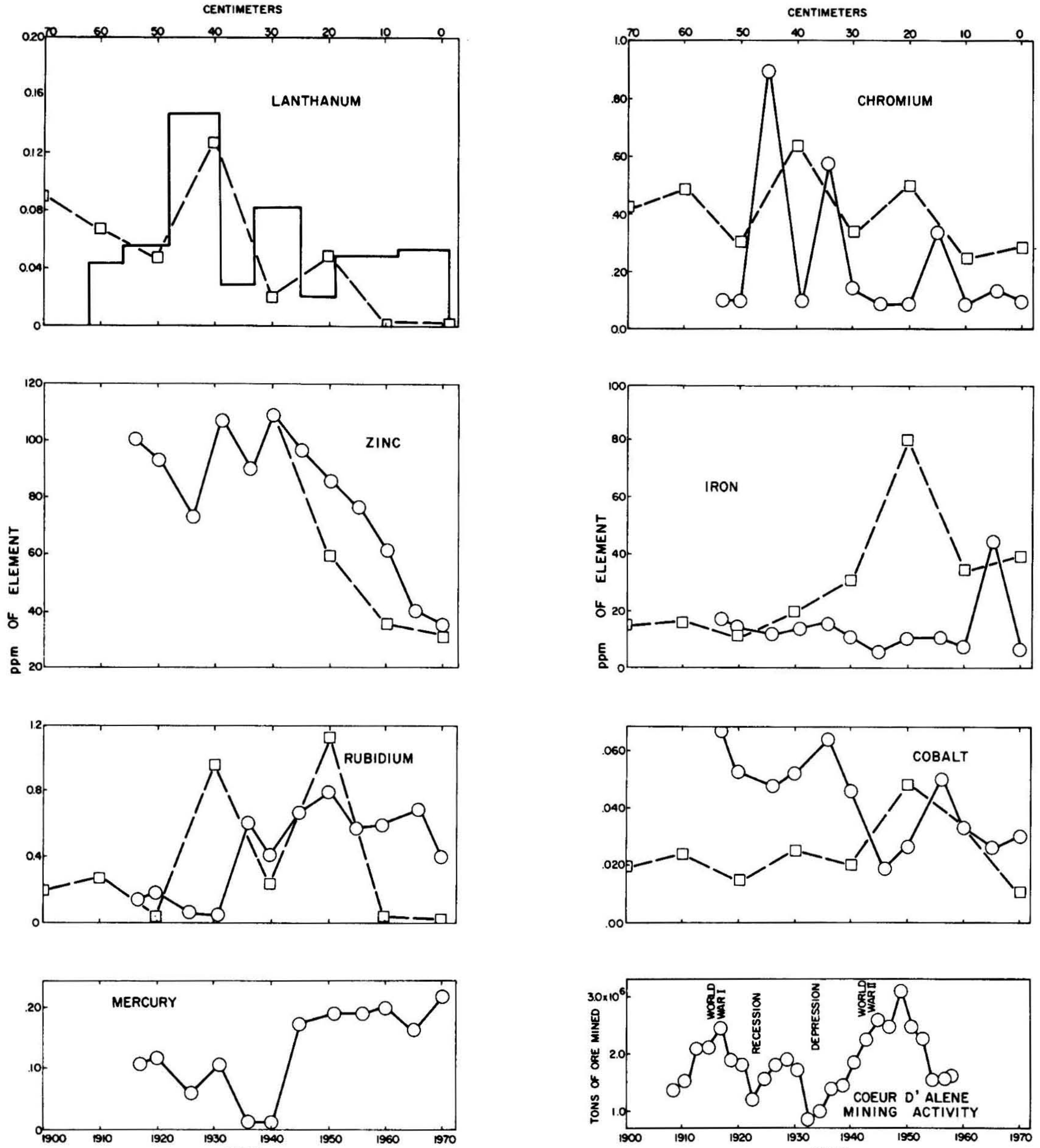

Figure 2. The solid lines represent μg of metal per gram of dry wood for the Corbin Park ponderosa pine tree and the dashed line are μg of metal per gram of dry Coeur d'Alene Lake sediment. Post Falls and Ross Point, La., data are used in the upper left corner of the figure. The historic mining data are shown in the lower right corner of the figure

Mercury concentrations in the Corbin Park tree increases with time and a minimum is observed which corresponds to the 1932–40 depression.

The Na, K, and Rb concentrations in the Corbin Park, Post Falls, and Ross Point trees increased significantly about 30–40 years ago. These data cannot be shifted to fit either the mining or the sediment data and suggest that other contributions, such as timber harvesting, sewage disposal, and so forth, probably account for the increase. The data are consistent with Ellis's observation (*9*) that trees growing near salt water have high Na concentrations.

The combined Mn data for the Post Falls and Ross Point trees roughly correlate with the mining data but do not agree with the sediment core data, which showed a recent maximum similar to iron. Since the Mn data represent six- to ten-ring (year) averages, some maxima could be averaged out. These data emphasize the advantages of sampling individual rings.

Except for the World War I peak, the Ag data follow the mining data by about four years. Antimony concentrations in the Post Falls–Ross Point composite also follow the mining data. With the exception of the pre-1932 maximum, Au also follows the mining data. The Sb and Au data are averages and composites and should be considered in the same category as Mn—that is, with reserve. The La data for the Post Falls–Ross Point composite show one large maximum which agrees with the sediment core data and indicate that a large La pulse passed through Coeur d'Alene Lake between 1920 and 1930. A smaller La pulse may have passed through in the 1940's.

The La and Fe data, shown in Figure 2, can be used with the sediment core data (*15*) to obtain a rough estimate of the recent sediment deposition rate for Coeur d'Alene Lake. These data indicate that the sediment deposition rate has been about 1 cm a year for the 1908–57 period. Since the Coeur d'Alene Lake cores are about 80 cm thick (*15*), approximately 80 years of mining and other environmentally significant human activities have taken place in the Coeur d'Alene region. It is noteworthy that mining operations started in the Coeur d'Alene region in 1888 (*17*).

These experiments are admittedly preliminary in nature, but they suggest that long-lived trees growing in intimate contact with rivers may be used to monitor variations of metal ion concentrations in rivers for times approaching a century. If allowances for holdup in Coeur d'Alene Lake are made, some of the metal concentrations correlated with the mining activity data. The research described here is analogous to attempts to correlate the ^{14}C content of tree rings with historic sunspot data (*18*), which is basically a signal-to-noise problem (*19*). Just as the sunspot correlation needs to be treated with reserve, so should the data reported here. Obviously, more research is necessary to establish the value of this method of monitoring metal concentrations of rivers. For example, the average yearly flow of the Spokane River was not considered in the analysis of the data. Another factor not considered was the background or precultural levels of these metals in the trees. These data could be obtained if longer-lived trees were sampled. The location of the tree should be carefully chosen to eliminate holdup in lakes. Future research should include these factors. If a 100-year-old tree growing in the Coeur d'Alene River had been used in this study, the time lag caused by holdup of Coeur d'Alene Lake would have been eliminated and, if river flow rates and background levels were included, regression analysis may have determined if a correlation actually does exist between metal concentrations in the trees and the river metal concentrations. Experiments are planned to test this hypothesis. Present data are not considered suitable for such an analysis.

Acknowledgments

This research was partially supported by the State of Washington and the U.S. Atomic Energy Commission [contract AT(45-1)-2221] (JCS) and the Office of Water Resources Research (WHF). We wish to acknowledge the assistance of G. Grant, G. Clifton, and T. Dillon for the neutron activation of the tree rings and Roy Filby, K. R. Shah, and P. F. X. Dunigan, Jr., for the use of the Coeur d'Alene Lake sediment data. We want to recognize the assistance of R. Rogers of the Idaho Game Department and G. Bailey, who obtained the tree cores used for this research.

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Concentration and Size of Trace Metal Emissions from a Power Plant, a Steel Plant, and a Cotton Gin

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■ An in-stack cascade impactor was used to determine the size distribution of particles, before and after emission control systems, of a coal-fired power plant, a steel plant, and a cotton gin. Samples were analyzed for total particulate matter and elemental metal content by graphite-furnace atomic absorption; Se was analyzed by neutron activation. A sharp decrease in the concentration and particle size was observed after the particulates passed through the control systems. Pronounced metal concentration and particle size relationships were found in the power plant and steel plant samples. The power plant outlet samples showed an increased concentration of Cr, Pb, Sb, Zn, and Se in the particle size range of 0–1 μm diameter. The particle removal efficiency of the baghouse and electrostatic precipitator control devices in this study was at least 98% for submicrometer sized particles.

Stationary emission sources can contribute significantly to the amount of primary particulate matter in air of anthropogenic origin, especially trace metals (*1, 2*). The effectiveness of particle control devices depends in large measure on the particle size of stack aerosols, yet, very little published information is available on the size distribution of particulates associated with stationary sources (*3, 4*). Particle size fractionating devices which can operate in a harsh stack environment have become available and should lead to a better understanding of particulate emissions (*5–7*). By applying methods similar to those used in determining the weight-size distribution of particles suspended in ambient air (*8*), we have used a Pilat impactor (*5*) to determine the weight size distribution of total particulate matter and trace metal components in several stationary emission sources. Samples were collected both before and after the emission control devices to assess the aerosol removal efficiency. The sources tested included a coal-fired power plant equipped with an electrostatic precipitator, a cotton gin equipped with a wet scrubber, and an electric arc furnace ferro plant equipped with a baghouse control system. These studies were carried out as part of a source testing program on best controlled industries for developing emission standards on new stationary sources.

Experimental Methods

Description of the Cascade Impactor. A University of Washington Mark III source test cascade impactor was used aerodynamically to size and collect aerosols within stacks of selected stationary sources (*9*). The impactor consists of seven stages and a backup filter to collect unimpacted particles, all of which are housed in a stainless steel cylinder that can be inserted into a stack or duct through a 10.2-cm (4-in.) port. The Mark III version differs somewhat from previous designs (*5, 10*) in that the airstream passes through the center of "donut" shaped collection surfaces rather than around openings near the walls to minimize wall losses. The sampler fractionates particles in the size range of about 50–0.5-μm diameter, expressed as spheres of unit density, depending on the flow rate that can be as high as 0.006 m^3/min (2.5 ft^3/min). The calibration curves used for each stage as a function of temperature and flow rate were determined by the manufacturer with polystyrene latex spheres of known dimension (*9*).

Aluminum disks cut to fit on top of each stage were weighed to the nearest microgram with a Mettler M-5 microanalytical balance; backup filters were similarly weighed after conditioning 24 hr below 50% relative humidity and room temperature. Because of high stack temperatures, glass fiber backup filters were used with the power plant and steel mill. Both membrane and glass fiber filters were used with the cotton gin although no difference in collection efficiency was observed. Particulate matter was impacted directly on the tared aluminum surfaces removed after sampling, folded, and returned to the laboratory for gravimetric and chemical analysis in much the same fashion as the ambient air studies conducted previously (*8*).

Field Operation. In the field, the sampler equipped with an appropriate vacuum source and flow measuring device (*9*) was inserted inside the stack and allowed to temperature equilibrate for 15 min with the sampling nozzle facing away from the air stream.

After temperature equilibration, the impactor was pointed toward the gas stream flow and a sample collected isokinetically at a point of average flue gas velocity for periods as short as 10 min or as long as 2 hr depending on the particulate loading. Sampling under isokinetic conditions was achieved by using an appropriate restriction at the inlet end of the impactor and by adjusting the flow rate with a variable speed vacuum pump. The velocity of the flue gas was monitored during sampling with a Pitot tube placed next to the impactor (*11*). The average sampling velocity was determined from the total volume of air sampled, corrected to dry standard volume units, and the total sampling time. By use of the size calibration curve provided by the manufacturer (*9*), the average stage constants were determined from the average flow rate and the approximate temperature of the flue gas. A particle size distribution curve was constructed on log-probability paper from the average stage constants and the cumulative percent mass (*5, 9*).

Chemical Analysis. In addition to gravimetric analysis of the collected particulate matter, metal constituents were determined on one set of samples collected before and after the control system by flameless atomic absorption spectrophotometry; neutron activation analysis was used to determine selenium in the power plant samples.

For analysis by flameless atomic absorption spectrophotometry, the aluminum collection surfaces and the filters were cut into strips, placed in individual Pyrex boats, and ashed in a Tracer Lab LTA 600 low-temperature asher for 30 min at 250 W with an oxygen flow of 80 cm/min. After it

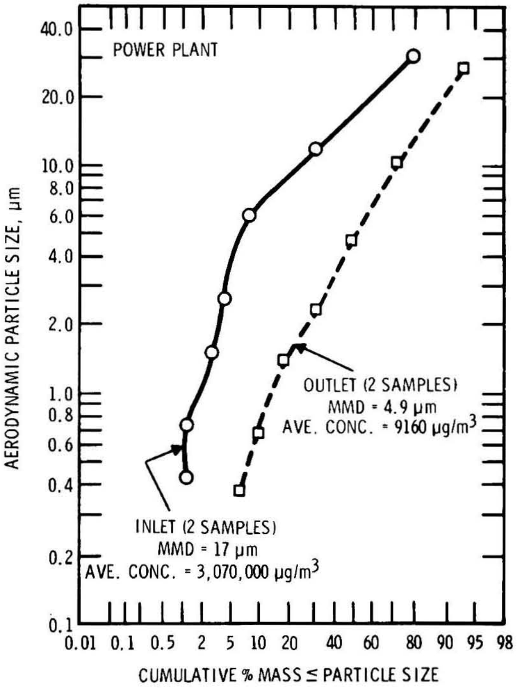

Figure 1. Composite mass size distribution of particulates collected before and after an electrostatic precipitator at coal-fired power plant

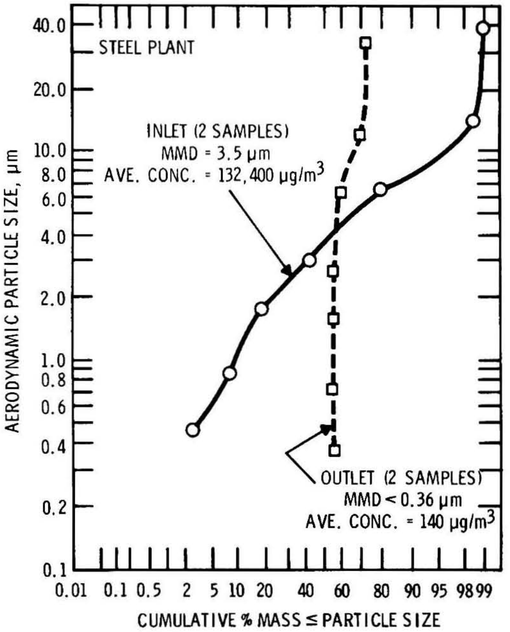

Figure 2. Composite mass size distribution of particulates collected before and after a baghouse at electric arc furnace steel plant

was ashed, each sample was removed and placed in a 20-ml beaker, 5 ml of 1:1 v/v HNO_3 added, and sonicated for 15 min at 50°C in a sonic cleaner. The supernatant was decanted into a 10-ml volumetric flask; the aluminum collection surfaces and filter strips were rinsed with distilled water that was also added to the volumetric flask. A final sample extract of 10 ml was used in the analysis. The following metals were analyzed using a Techtron AA-5 atomic absorption spectrophotometer equipped with a graphite furnace: Fe, V, Cd, Cr, Co, Ni, Mn, Cu, Pb, Sb, and Zn.

Stationary Source Tested. The sources tested included a coal-fired power plant in Illinois, a cotton gin in California, and an electric arc ferro plant in Pennsylvania. At least two samples were collected both before and after the control devices.

The power plant fired 60 tons (54,432 kg) of coal per hour for a unit generation of 105 MW. The stack gas flow rate was 257,000 dry standard cubic feet per minute (DSCFM), equivalent to 7273 m³/min. The control device was a 64-plate electrostatic precipitator with a ratio of collecting plate area to gas flow of 391. The design specifications for the precipitator were 1.5 grain (97.2 mg) per DSCFM on the inlet and 0.005 grain (0.3 mg) per DSCFM on the outlet for an efficiency of 99.7%.

The ferro plant operation consisted of two electric arc furnaces with capacities of 75 and 50 tons (68,040 and 45,360 kg) per day. The batch process involved meltdown, oxidizing, slagging, and refining steps with each cycle consuming 6–8 hr. Two 900-hp fans removed the effluent gases from the shop area through adjoining openings in the shop roof and through a single exhaust duct and to a 12-compartment baghouse. The volumetric flow rate at the outlet stack tested was 78,000 DSCFM (2207 m³/min). The total average gas flow rate through all six outlet stacks was 454,000 DSCFM (12,848 m³/min). The effluents are exhausted to the atmosphere from the baghouse through six 9-ft (2.74 M) diameter stacks. During sampling, the shake cycle on the baghouse control device was ignored.

The cotton gin operated continuously producing an average of 600 bales per day, each weighing approximately 500 lb (227 kg). Mechanical unloading of the cotton was made directly from wagons brought in from the field. The cotton was sent to driers for moisture adjustment and to cleaners for elimination of field debris. Successive stages of operation removed seeds and lint. Finally, the cotton was processed through the battery condenser and then the baling press. The sampling site chosen was the inlet and outlet of the wet scrubber that received the effluent from the battery condenser. The outlet flow through the scrubber duct was 16,000 DSCFM (453 m³/min); the air from the scrubber was piped back into the plant area.

Results and Discussion

Size Distribution of Total Particulates. The size distributions of total particulate (TP) matter for each stationary emission source tested are shown in Figures 1 through 3. The distribution curves represent a composite of data from at least two Pilat impactor samples collected before and after the control devices. Although the samples were not collected simultaneously downstream and upstream from the control system, sampling was carried out during the same day and during the same process operation.

In general, the size distribution curves for the three sources tested were not entirely well described by a log-normal function. The inlet samples for the power plant and the steel mill, Figures 1 and 2, exhibited some evidence of bimodality. For all three sources, the particle concentration and the median particle size were reduced after the aerosol passed through the control device.

An estimate of the total quantity of particulate matter

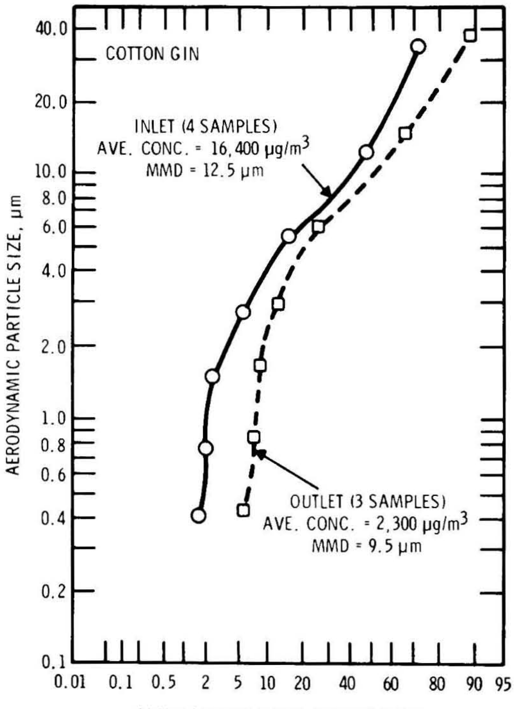

Figure 3. Composite mass size distribution of particulates collected before and after a wet scrubber at a cotton gin

emitted from each source can be determined from the concentration per unit volume and the total volume of outlet gas given in the Experimental Methods. For example, the power plant emitted 2364 g/min, the steel plant 11 g/min, and the cotton gin 37 g/min. The size distribution curves can provide further information on the concentration of particulate emissions as a function of size. For example, particles having an aerodynamic size less than or equal to 1-μm diameter, as spheres of density one, range from 284 g/min for the power plant, 70 g/min for the steel plant, and 2 g/min for the cotton gin. It is clear that the power plant represents the most important stationary emission source of the three tested, especially in view of the large amount of submicrometer size aerosol emitted.

The data provided in Figures 1 through 3 can also be used to assess the efficiency of the control systems on each source. Overall efficiency for total particulate matter was 99.7% for the power plant equipped with an electrostatic precipitator, 99.6% for the steel plant equipped with a baghouse, and 86% for the cotton gin equipped with a wet scrubber. The removal efficiency as a function of particle size, can be calculated from the figures and appears to decrease with decreasing particle size. For example, for the particles less than or equal to 1-μm diameter, the removal efficiency dropped to 98.0% for the electrostatic precipitator, remained about the same, 99.3%, for the baghouse, and dropped substantially to 47.3% for the wet scrubber. The particle removal efficiency of the baghouse and the precipitator determined in this study agrees well with results presented by Craig (*12*). He found a removal efficiency for 1-μm diameter particles of 95% for an electrostatic precipitator and 99.7% for a baghouse.

Concentration Measurements of Metal Constituents. The concentration and mass median diameter (MMD) of metal-containing constituents for both the control system inlet and outlet of each source tested is summarized in Table I. Iron represented the major constituent in both the inlet and the outlet samples from the power plant. Other metals detected included V, Cd, Cr, Ni, Pb, Sb, Zn, and Se. Mn was found in relatively high concentration in the inlet sample but not detected in the outlet. It is likely that the large size of the Mn-containing particles accounted for its virtually complete removal by the electrostatic precipitator. With the exception of Se, TP and the metals measured decreased in median particle size after passing through the control system, probably because the larger metal-containing particles were more efficiently removed. It is especially disturbing that Se was detected in relatively large quantities representing an emission rate of approximately 1.7 g/min.

Table I. Concentration and Mass Median Diameter of Particulate Components from Stationary Emission Sources

	Power plant				Steel mill				Cotton gin			
	Inlet		Outlet		Inlet		Outlet		Inlet		Outlet	
Component	Concn, μg/m³	MMD, μm	Concn, μg/m³	MMD, μm	Concn, μg/m³	MMD, μm	Concn, μg/m³	MMD, μm	Concn, μg/m³	MMD, μm	Concn, μg/m³	MMD, μm
					Sample Set A							
TP	38×10^5	18	8700	4.7	86,700	5.5	92	<6	18,700	13	2080	8.8
Fe	3×10^5	6	1340	2.6	51,180	5.1	[a]	[a]	[a]	[a]	[a]	[a]
V	970	5	1.5	1.6	34	4.8	0	0	14	1.2	9	2.1
Cd	8.5	8.4	0.1	5.0	0	0	0	0	0	0	0	0
Cr	300	12	0.7	<0.5	1,290	4.0	1.2	26	3	0.7	0	0
Co	0	0	0	0	0	0	0	0	5	0.7	0	0
Ni	395	11.2	1.3	5.4	45	<5	0	0	14	0.8	0	0
Mn	600	15	0	0	7,130	3.0	3.2	11.3	41	0.8	0	0
Cu	[a]	[a]	[a]	[a]	185	3.3	0	0	100	0.8	0	0
Pb	189	5	1.4	1.1	960	2.6	2.3	>30	23	0.8	0	0
Sb	689	<1	6.8	0.6	5	15	0	0	41	0.7	0	0
Zn	162	8.6	0.7	4.7	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
					Sample Set B							
TP	23×10^5	16	9600	4.7	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Se	114	0.9	6.5	4.7	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]

Set A analyzed by graphite furnace atomic absorption. Set B analyzed by neutron activation.

[a] Component could not be reliably distinguished from background material in the blank collection surfaces. [b] Not analyzed.

Table II. Percent Particle Mass as Function of Size

Coal-fired power plant[a]

	Sample set A																				Sample set B			
	Total particulate		Fe		V		Cr		Ni		Mn		Pb		Sb		Cd		Zn		Total particulate		Se[b]	
Size range, μm	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Above 30	24	5	15	8	6	0	16	0	40	0	0	0	18	0	0	0	12	12	15	2	21	5	7	8
20–30	21	6	6	5	7	0	14	0	4	0	8	0	6	0	0	0	11	8	6	6	19	6	5	6
10–20	38	17	15	9	17	12	26	0	18	13	89	0	20	1	0	0	22	10	21	30	31	18	9	16
5–10	13	20	16	14	20	10	7	0	23	43	33	0	6	9	0	0	15	20	26	10	19	19	19	18
1–5	3	38	30	45	31	43	25	20	7	30	0	0	29	40	0	38	5	30	17	8	7	37	9	22
0–1	1	14	18	19	19	35	12	80	8	14	0	0	21	50	100	62	35	20	15	44	3	15	51	30

[a] Samples collected at the inlet and at the outlet of an electrostatic precipitator control device. [b] Analysis by neutron activation.

Iron was also the major metal constituent in the steel plant inlet sample (Table I); however, the highly efficient baghouse control removed detectable quantities in the outlet sample. Although quantities of V, Cr, Ni, Mn, Cu, Pb, and Sb were found in the inlet sample, only trace amounts of Cr, Mn, and Pb passed through the control system. The periodic bag-shaking or cleaning operation which probably emits conglomerated particles may account for the increase in size of the Cr-, Mn-, and Pb-associated particles.

Detectable quantities of V, Cr, Co, Ni, Mn, Cu, Pb, and Sb were found in the inlet cotton gin sample, but only V was detected in the outlet sample. It is likely that most of the metals found were natural constituents of the cotton although several may have been associated with pest control agents.

Size Range of Metal Particulates. Two recent reports by Lee and vonLehmden (*1*) and Natusch et al. (*13*) have suggested that the concentration of metals in particulates from coal-fired power plants have a pronounced dependence on size. Fly ash samples aerodynamically size-fractionated and chemically analyzed showed that Fe and Al predominate in large particles but that Pb, Cd, Cr, Ni, Mn, Sb, Se, Zn, and V predominate in smaller size particles.

Table II presents a summary of the metal constituents measured in six particle size ranges for the coal-fired power plant tested in this study. A general decrease in particle size was observed after the metal aerosol passed through the electrostatic precipitator. Several metals emitted past the control device were predominantly in the 0–1-μm diameter size range including Cr, Pb, Sb, Zn, and Se. Total particulate Cd, Fe, and V were in the 1–5-μm diameter range while Ni was predominantly in the 5–10-μm range. Mn appeared to be effectively removed by the control device. Although the data on Cr, Pb, Sb, Zn, and Se agree well with the fly ash studies (*1, 13*) the size relationships of Fe, Cd, V, and Ni are not so pronounced as the fly ash studies.

Table III presents a similar compilation of metal constituents in various size categories for the steel plant tested. Results are quite dissimilar than for the power plant data given in Table II. Although the total particulate size was markedly reduced after passing through the baghouse control system, Cr, Mn, and Pb in the outlet sample appeared to be concentrated in particles larger than 10 diameter. Particles containing V, Ni, Cu, and Sb appeared to be completely removed by the baghouse. The baghouse control system appeared to be especially effective in removing particles below 5 μm diameter.

A summary of the metal-particle size relationships found in the cotton gin samples is given in Table IV. Except for V, the metal-containing particles were effectively removed by the wet scrubber control system. The scrubbing efficiency was somewhat surprising in view of the fact that many of the metal-containing particles on the inlet side were in the 0–1-μm diameter size range—e.g., Cr, Ni, Mn, Cu, Pb, Sb, and Co. In the inlet samples, the measured elemental metal content was only 1.3% for the cotton gin compared to 3.5% for the power plant and 70% for the steel plant as calculated from the data in Table I.

Source of Errors. The harsh environment associated with a stationary emission source can have a pronounced effect on sampling accuracy. It is not uncommon to have mass concentration measurements in stacks vary by 20% or more. In this study, samples were extracted from a point of average velocity; however, small changes in the volume gas flow could have occurred during sampling thereby diminishing the accuracy of results.

It is likely that the greatest source of errors are associated with the cascade impactor. All impactors suffer from inherent problems, discussed by Ranz and Wong (*14*) and by Lee (*15*), and include loss of particles on impactor walls, particle bounce-off and reentrainment, and inaccuracies of calibration. Berner (*16*) pointed out that the adhesiveness of particles impacted on the University of Washington sampler depends in large measure on the chemical nature

Table III. Percent Particle Mass as Function of Size

Electric arc furnace steel plant[a]

	Total particulate		Fe		V		Cr		Ni		Mn		Cu		Pb		Sb	
Size range, μm	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Above 30	1	28	0	[b]	0	0	0.5	46	0	0	0.2	14	0	0	0	58	0	0
20–30	1	3	0	[b]	1	0	0.5	13	0	0	0.4	6	0.6	0	1	0	0	0
10–20	11	3	11	[b]	15	0	6	21	0	0	7.4	60	3.4	0	17	7	100	0
5–10	34	7	41	[b]	30	0	39	14	0	0	40	20	14	0	17	13	0	0
1–5	45	2	36	[b]	54	0	50	0	100	0	46	0	72	0	44	0	0	0
0–1	8	57	12	[b]	0	0	4	6	0	0	6.0	0	0	0	21	22	0	0

[a] Sample collected at the inlet and at the outlet of a baghouse device. [b] Component could not be reliably distinguished from background material n the blank collection surfaces.

Table IV. Percent Particle Mass as Function of Size

Cotton gin[a]

Size range, μm	Total particulate		V		Cr		Ni		Mn		Cu		Pb		Sb		Co	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Above 30	12	24	0	0	0	0	0	0	6	0	0	0	0	0	0	0	0	0
20–30	6	9	1	2	0	0	0	0	1	0	0	0	0	0	0	0	0	0
10–20	32	29	19	14	0	0	0	0	1	0	0	0	0	0	0	0	0	0
5–10	29	23	1	8	0	0	0	0	1	0	0	0	0	0	0	0	0	0
1–5	16	14	43	56	15	0	7	0	24	0	6	0	5	0	7	0	5	0
0–1	5	1	36	20	85	0	93	0	67	0	94	0	95	0	93	0	95	0

[a] Sample collected at the inlet and at the outlet of a wet scrubber control device.

of the particles and the quantity of deposit on the impaction surface. Wall losses that can range from 30–50% of the total catch (*17*) can greatly reduce the sample collection efficiency, thereby presenting the most serious known error. Therefore, the concentration data presented here should be considered perhaps 50% less than the true value. Particle reentrainment evidenced by trailing around the points of impaction did not seem to be a problem in the sources tested.

The sampler was calibrated with polystyrene latex spheres by the manufacturer (*9*). Inaccuracies in the calibration method can arise from reentrainment of the calibration aerosol and the possible formation of aggregates (*18*). Despite these possible sampling problems, a recent presentation by Bird and Harris (*19*) indicated that remarkably good comparative results can be obtained with available cascade impactors for stack sampling, including the University of Washington impactor used in this study.

Errors in the chemical analysis are mainly associated with the completeness of extraction, presence of interfering components, and instrumental inaccuracies. High sensitivity and specificity can be obtained with graphite furnace atomic absorption and neutron activation analysis. Limited cross-checking of these analytical methods with duplicate samples showed comparisons within ±15%. Incomplete extraction of the collected sample is probably the greatest unestimated analytical error.

Conclusions

Metal-containing particulate emissions from coal-fired power plants and steel plants can contribute a sizable proportion of the trace metal burden in the atmosphere. A pronounced relationship was observed between metal concentration and particle size in the sources tested, especially for the power plant samples where Cr, Pb, Sb, Zn, and Se were predominantly concentrated in particles between 0- and 1-μm diameter. Potential sources of error in this study are mainly associated with the accuracy of the sampling methodology and include wall loss effects, particle reentrainment, and calibration inaccuracies.

The authors believe that more studies of this type are certainly needed to more fully assess the importance of trace metal emissions from stationary sources. The recent work of Gordon et al. (*4*) is especially significant in relating atmospheric particulate levels to specific emission sources.

Acknowledgment

The authors thank Peter Lambert for carrying out the selenium analysis. We also wish to acknowledge the assistance given by Robert Ajax and his staff for their help in the sampling portion of this study and to Darryl von Lehmden for the many helpful comments and suggestions during many phases of the work.

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Received for review April 12, 1974. Accepted January 23, 1975. Mention of commercial products is for identification only and does not constitute endorsement by the Environmental Protection Agency of the U.S. Government.

Reactivities of Complex Hydrocarbon Mixtures

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■ Complex hydrocarbon mixtures in the presence of NO_x were reacted for several hours in a large irradiation chamber. The hydrocarbons were reacted at concentrations of 5, 10, and 20 ppmC in mixes containing ½ or 1 ppm NO_x. Rates of oxidation of nitric oxide, nitrogen dioxide dosage, hydrocarbon consumption, eye irritation, and yields of peroxyacetyl nitrate, formaldehyde, and oxidant were measured. The results suggested that if aromatics are substituted for olefins in a hydrocarbon mixture, a decrease in both oxidant and PAN dosages occurs. Eye irritation increased with increasing aromatics. These reactivity parameters decreased by replacing aromatics with paraffins.

Present control strategies for oxidant and related air quality standards are concerned with the role of hydrocarbons in facilitating oxidant control. However, such strategies are based upon assumptions that the present hydrocarbon composition will be maintained and perhaps the present HC /NO_x ratio as well. Previous laboratory chamber studies have shown that different hydrocarbons as well as different HC/NO_x ratios, show wide variations in oxidant formation (*1–3*). Studies have shown that not only is the HC/NO_x ratio altered with the new vehicles, but that the hydrocarbon composition is altered when exhaust is catalytically treated (*4*). If automotive hydrocarbon emissions are to be catalytically removed, lead-free gasoline is required. A reduction in lead content in fuel could result in fuel compositional changes—i.e., increases in aromatics or increase in substitution in paraffins if the octane number is to be maintained. Changes in fuel composition have been associated with changes in automotive exhaust and subsequently the reactivity of auto exhaust (*2, 5*).

Methods have been proposed for calculating the photochemical reactivities of hydrocarbon emissions (*2, 3, 6*). Although these methods give qualitative directions in reactivities, the magnitude of the effect can best be determined in smog chambers with real hydrocarbon mixtures.

This study was undertaken to delineate what effect hydrocarbon compositional changes would have on smog manifestations. Both the hydrocarbon distribution—i.e., percent aromatic, olefinic, and paraffinic contents as well as the NO_x effect have been investigated.

Experimental

The experimental techniques employed in this study were those in vogue between 1969–71—the period in which this study was performed.

The hydrocarbon mixture employed is shown in Table I. It was composed of acetylene, five paraffins, six olefins, and five aromatics. The proportions were such that the early morning traffic peak at Los Angeles was simulated (*7*). Table II shows the comparison of the simulated chamber mix to the atmospheric samples collected in Los Angeles. The average hydrocarbon in the paraffin mix is a C_5 (C = 4.8); for the olefins a C_3 (C = 2.9), and for the aromatics a C_8 (C = 8.3). Therefore, 10-ppm C of a paraffinic mix would contain the equivalent of 2.08 ppm (v/v) of compound while an olefinic mix would contain 3.45 ppm (v/v). An aromatic mix would contain 1.20 ppm (v/v) of compound. When the mixture was studied separately—i.e., just the paraffins or the olefins—the same five paraffins, six olefins, and five aromatics were studied. Thus, an olefin mixture would contain all of the olefins shown in Table I without the paraffins and the aromatics.

The ultraviolet radiations of the hydrocarbon–NO_x mixtures were carried out in a 335-ft^3 aluminum chamber equipped with polyvinyl fluoride film windows (*8*). This chamber was equipped with fluorescent blacklights and sunlights located externally. The k_d value for the chamber was 0.4 min^{-1} (*9*). The light intensity was periodically measured by a Dark Ray Meter (Ultraviolet Product Co.). When low meter readings were obtained, one quarter of the light bulbs would be replaced. A further check of the light intensity was done by running a hydrocarbon (propylene) periodically. Some of our recent modeling studies of the NO_2 photodissociation in nitrogen suggests that the irradiation of NO_2 in nitrogen for short periods (30 sec to 1

Table I. Simulated Los Angeles Atmospheric Mix

Compound	Ppm of C
Paraffins and acetylene	
Acetylene	0.53
Isopentane	0.86
n-Pentane	1.43
2-Methylpentane	0.51
2,4-Dimethylpentane	0.48
2,2,4-Trimethylpentane	0.61
Aromatics	
Toluene	0.98
m-Xylene	0.72
n-Propylbenzene	0.54
Secondary butylbenzene	0.60
1,2,4-Trimethylbenzene	1.11
Olefins	
Butene-1	0.16
cis-2-Butene	0.17
2-Methyl-1-butene	0.13
2-Methyl-2-butene	0.16
Ethylene	0.72
Propylene	0.29

Table II. Composition of Chamber Mix and Atmospheric Samples

	Percent compn (carbon basis)			Av no. of carbon atoms/compd		
	Nominal chamber mix	Dola[a] 7–8 a.m., 1968	Dola 2nd St. Tunnel, 1970	Nominal chamber mix	Dola 7–8 a.m., 1968	Dola 2nd St. Tunnel, 1970
Σ Paraffins + acetylene	45	57	49	4.8	4.7	5.1
Σ Olefins	15	11	13	2.9	3.4	3.1
Σ Aromatics	40	32	38	8.3	8.2	8.1

[a] Dola = downtown Los Angeles.

min), followed by measuring the NO_2 after turning off the lights is unsatisfactory as a measure of light intensity. This arises from dark reactions oxidizing NO back to NO_2 in the gas phase. Our modeling efforts with 5-ppm NO_2 and a $K_a\Phi$ value of 0.15 min^{-1} ($K_a\Phi = k_d/1.5$) show that a 15% error on the low side is made in the k_d value if NO_2 is measured as much as 5 min after the lights are turned off (an operation usually employed with wet chemical methods). In this study, the k_d value was measured from $t = 0$ to $t = 5$ min every minute on a continuous basis. The errors introduced by this technique should be minimized. However, since slow colorimetric wet chemical techniques were used in this study, the exact k_d value may be slightly higher than the report value of 0.4 min^{-1}. Unfortunately, the chamber of this study is no longer in existence and the true k_d value cannot be remeasured with the use of faster responding chemiluminescent NO_2 detectors. The chamber was preheated with infrared lamps before the start of the irradiations and operated at 32 ± 1°C at a relative humidity of approximately 33%. Chamber air was prepared by introducing ambient air cleaned by passage through activiated charcoal and particulate filters. The gaseous reactants were charged directly into the chamber by calibrated syringes. Known quantities of liquid reactants were introduced into the chamber by vaporizing into a heated glass line while flushing into the chamber by either air or nitrogen.

Nitrogen dioxide was analyzed colorimetrically (*10*). Nitric oxide was analyzed as nitrogen dioxide after oxidation with potassium dichromate paper (*11*).

Oxidant was determined manually by the colorimetric 1% neutral potassium iodide method (*12*). Interferences from PAN (peroxyacetyl nitrate) and NO_2 were considered and corrections were introduced when oxidant was recorded. A 48% response of PAN and a 15% response of nitrogen dioxide relative to ozone were obtained with the KI reagent. No corrections were made for any other oxidants with this reagent. However, since other oxidants usually require a long period to react with the KI reagent, their interferences would be minimized (*13*). Nitrogen pentoxide was not tested for interference.

The light olefins were analyzed by means of a gas chromatograph equipped with a dibenzyl ether column on silica gel. The paraffins and butenes on a capillary column coated with squalene. The oxygenates and aromatics were separated by a 1,2,3-tris(2-cyanoethoxy)propane column. PAN and methyl nitrate were separated on a borosilicate column packed with carbowax 500 on Gas ChromZ and were measured on an electron capture detector. Attempts to analyze for peroxybenzoyl nitrate by analogous techniques were unsuccessful.

Formaldehyde was analyzed by means of the chromotropic acid method as applied to atmospheric systems (*14*).

Results and Discussion

The reactivities of a large number of hydrocarbons in terms of oxidant formation, NO oxidation, and hydrocarbon oxidation, have been determined by a number of investigators (*15–18*). Reactivity assignments are valuable from the standpoint that selective controls of hydrocarbons can be considered for air pollution control strategies.

In Table III are shown the molar reactivity measurements of the test mixtures. This table shows that on a carbon basis almost every reactivity parameter is greatest with the olefin mix. On a ppm-molar basis (Table IV) the reactivity parameters are greatest with the aromatic mixes, reflecting, in part, the higher molecular weight of the aromatics.

Table III. Reactivity Measures for Individual Classes of Hydrocarbons

10 Ppm of C + 0.50 ppm of NO_x

	Atmospheric mix		Paraffin mix	Aromatic mix	Olefin mix
	Obsvd	Calcd			
5-Hr oxidant dosage, ppm × min	138	78	24	118	134
Oxidant maximum pphm	67(190)[a]	41	37(>300)[a]	50(109)[a]	63(60)[a]
5-Hr PAN dosage, ppm × min	37	29	<2	45	76
5-Hr NO_2 dosage, ppm × min	35	62	100	6	20
Time to oxidize 0.40 ppm of NO, min	42		134	29	10
HC consumed in 5 hr, ppm of C	3.7		1.4	5.8	8.1
Formaldehyde yield, ppm	0.45	.37	0.17	0.30	1.20
Eye irritation index	0.6	.50	0.3	0.6	0.8

[a] Time for the maximum to occur in minutes.

Table IV. Molar Reactivity Measures for Individual Classes of Hydrocarbons

10 Ppm of C + 0.5 ppm of NO_x

	Reactivity/ppm compd		
	Paraffin mix	Aromatic mix	Olefin mix
5-Hr oxidant dosage, ppm × min	11.5	98.5	38.8
5-Hr PAN dosage, ppm × min	0.7	37.5	22.0
5-Hr NO_2 dosage, ppm × min	48.1	30.0	5.8
Time to oxidize 0.40 ppm of NO, min	64.4	24.2	2.9
HC consumed in 5 hr, ppm of C	0.67	4.83	2.35
Formaldehyde yields, ppm	0.08	0.25	0.35
Eye irritation index (0–5 scale)	0.14	0.50	0.23
Maximum oxidant, pphm	17.8	30.8	18.3

A linear summation method (*19*) was attempted in order to calculate reactivity of a mixture on the basis of reactivities compiled for the individual mixes. These values are shown in column 2 of Table III. It is noted that the observed reactivity parameters are in every case greater than those predicted by the linear summation method. A plausible explanation for the lack of agreement between columns 2 and 3 in Table III may arise, at least in part, from the increase in reactivity of the paraffins. In most chamber runs, the NO_2 maximum occurs late in the run—i.e., in Table III for 90% of the NO to oxidize, 134 min were required for paraffins while only 29 min were needed for the aromatics and 10 min for the olefins. Since the atmospheric mixture contains paraffins, olefins, and aromatics, the oxidation rate of NO would increase, thus exposing paraffins early in the reaction to high concentrations of NO_2. Such a system is much more reactive because of the absence of NO inhibition (*17, 18*), and the photolysis of NO_2 would result in either O_3 formation or direct attack of 0 atoms onto the hydrocarbon. For this reason, the reactivity measures for the paraffins (column 3) and to some extent those shown for aromatics (column 4) in Table III are not applicable. Consequently, the relative reactivities of hydrocarbons and other organics should be measured at the stage of reaction that will reflect the maximum potential for the reaction.

Oxidant Yield

The oxidant yield, both dosage and maximum, in the paraffin–NO_x system is greatest when the HC/NO_x ratio is quite large. Thus, at a HC/NO_x ratio of less than 10/1, there is very little ozone produced during the 300-min irradiation (Figure 1). This is borne out by the fact that the time for the NO_2 maximum is very close to the time limit set for the experiments. Since NO is still present in these runs, little or no ozone is expected ($NO + O_3$ reaction). The highest oxidant dosages were observed at the highest HC/NO_x ratio—i.e., 77/1. This was at the lowest NO_x concentration (~0.13 ppm). The formation of high oxidant at low NO_x concentrations does not preclude the formation of oxidant at higher concentrations of NO_x if the irradiation time had been increased in the 10-ppm C–0.5-ppm NO_x cases. In a 10-ppm C (the $NO_x = 0.5$ ppm), the ozone curve at the conclusion of the run—i.e., 300 min had a slope of 4.4×10^{-1} pphm/min. In another 10-ppm C run (the lower NO_x value of 0.1 ppm), the slope at 300 min is only 4.6×10^{-2} for the same time. The slope of the higher NO_x-containing system was almost an order of magnitude greater.

The maximum ozone dosage for the olefin–NO_x system occurs at a HC/NO_x ratio of 10/1 under the experimental conditions studied. However, the HC/NO_x range is too narrow to definitively establish what HC/NO_x ratio is most favorable for maximum ozone dosage. An earlier study by Altshuller et al. (*20*) suggested that the maximum ozone is produced at a ratio of ~6/1 for propylene–NO_x system.

The oxidant dosages of the olefin–paraffin, aromatic–paraffin, olefin–aromatic, and the paraffin–olefin–aromatic systems are shown in Figures 2–5. Figure 2 shows that the

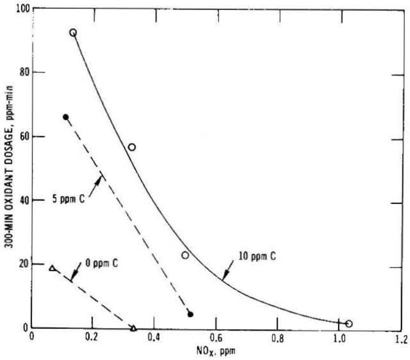

Figure 1. Effect of NO_x concentration on oxidant dosage from paraffin mixes

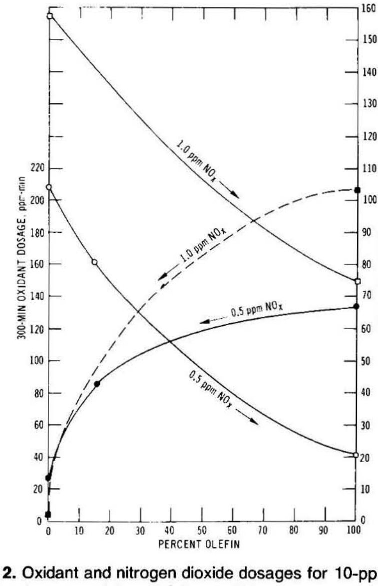

Figure 2. Oxidant and nitrogen dioxide dosages for 10-ppm C olefin–paraffin mixtures at 1.0- and 0.5-ppm NO_x

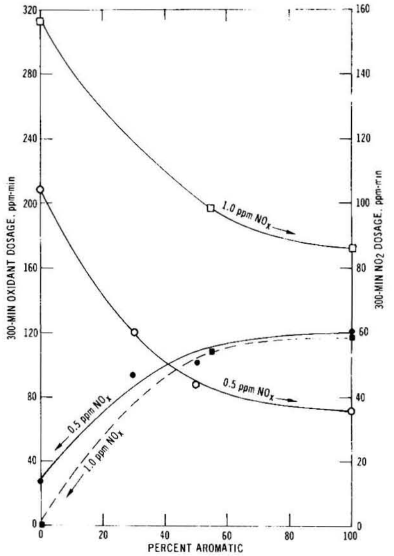

Figure 3. Oxidant and nitrogen dioxide dosages for 10-ppm C aromatic–paraffin mixtures at 1.0- and 0.5-ppm NO_x

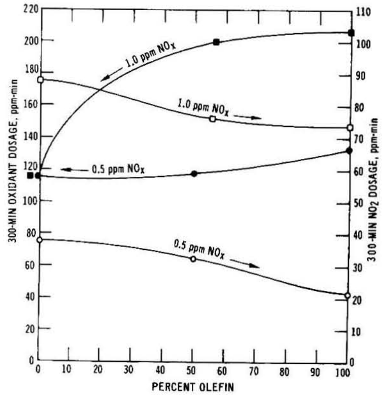

Figure 4. Oxidant and nitrogen dioxide dosages for 10-ppm C olefin–aromatics mixtures at 1.0- and 0.5-ppm NO_x

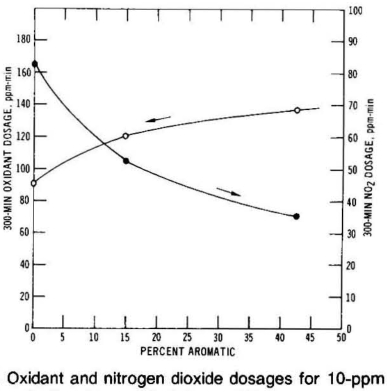

Figure 5. Oxidant and nitrogen dioxide dosages for 10-ppm C simulated atmospheric mixture with 0.5-ppm NO_x

oxidant dosage increases as the olefin content is increased in the olefin–paraffin mixture at two different NO_x levels. When aromatics are added to paraffins (Figure 3), the 300-min dosage increases, then appears to level off at about 60% aromatic for both the 0.5- and 1.0-ppm levels of NO_x. The olefin–aromatic mixture, Figure 4, shows that the oxidant dosage increases with increasing olefin although the increase is not very great. The oxidant dosage increases from approximately 115 ppm × min to 133 ppm × min for 0–100% olefin for 0.5 ppm NO_x. For the 1.0-ppm NO_x, the increase is from 120–208 ppm × min with the bulk of the increase occurring with the first 50% of the olefin.

The oxidant dosage for 10-ppm C and 0.5-ppm NO_x is shown in Figure 5 for the simulated atmospheric mix. As with Figure 3, the replacement of paraffins with aromatics shows that the oxidant dosage increases. In Figure 6 are shown the data for oxidant dosages obtained from the simulated atmospheric mixture at different HC and NO_x concentrations. At the low NO_x levels—i.e., ~0.1 ppm, it is noticed that an average of 15 ppm × min of oxidant is produced in the chamber after 300-min irradiation in the absence of hydrocarbons. This aspect has been attributed to contaminates coming off the walls of a dirty chamber (*21*). With 0.3 ppm of NO_x, there is sufficient NO to suppress oxidant formation in spite of dirty chamber conditions. With 10-ppm C, the oxidant dosage apparently reaches a maximum at ~75 pphm of NO_x (Figure 6). At the 5-ppm C, the oxidant dosage appears to decrease after reaching a maximum at a NO_x of 0.5 ppm. With increasing NO_x, the oxidant dosage decreases. This is probably a result of NO inhibition (*17, 18*).

It is interesting to compare the oxidant dosages arising from the paraffinic and atmospheric mixes at different HC and NO_x levels. In Table V are shown the data for such a comparison. The paraffinic mixes produce more oxidant than the atmospheric mix when the NO_x levels are very low.

NO_2 Yield

The NO_2 dosages are shown in the same figures that contain the oxidant dosages. In every case, the NO_2 dosage decreases with increasing oxidant. This necessarily follows since the earlier the NO_2 maximizes, the earlier NO is removed and oxidant is produced. In the presence of ozone, the NO_2 can be further oxidized to N_2O_5 and subsequently removed from the chamber by reacting with H_2O on the walls of the chamber (*22*).

The fate of NO_x in these systems is unknown since PAN and methyl nitrate are the only significant NO_x-containing products that can be measured. In a typical run containing 5-ppm C of olefins with NO_x of 52 pphm, after 300 min of irradiation, there remained ~4.5 pphm of NO_2, 6 pphm of PAN, and 4 pphm of $MeONO_2$. This accounts for only 28% of the starting NO_x. The remaining 72% is probably oxidized to nitric acid on the walls of the chamber.

Hydrocarbon Reaction and Carbon Balance

In most cases the carbon balance in these systems is poor. In the paraffin (10 ppm of C) with the 0.5-ppm NO_x system, one of the best carbon yields was obtained. With 1.4-ppm C of paraffin reacted, 10-pphm C of formaldehyde, 10-pphm C of acetaldehyde, 15-pphm C of propionaldehyde, 40-pphm C of acetone, 4.8-pphm C of PAN, and 2.8-pphm C of $MeONO_2$ were observed. This accounts for 59% of the carbon. In the olefin–NO_x (HC/NO_x = 10/0.5) system with 9.78 ppm of carbon consumed, the products observed were formaldehyde–130-pphm C, acetaldehyde–68-pphm C, propionaldehyde–44-pphm C, acetone–52.5-pphm C, PAN–43.6-pphm C, $MeONO_2$–0.3-pphm C, and methyl ethyl ketone–68-pphm C. This accounts for ~46% of the carbon consumed. The aromatic–NO_x mixtures had the worst carbon balance. With 6.3-ppm C of aromatic reacted only 13% of the carbon could be accounted for as formaldehyde (35 pphm of C), acetaldehyde (10 pphm of C), acetone (8.8 pphm of C), and PAN (28 pphm of C). No aromatic aldehydes could be detected. In the mixture containing paraffins, aromatics, and olefins, the products could account for 38% of the carbon. The products included formaldehyde–44-pphm C, acetaldehyde–20-pphm C, propionaldehyde–20.5-pphm C, acetone–33-pphm C, PAN–30-pphm C, $MeONO_2$–pphm C, and MEK–10-pphm C.

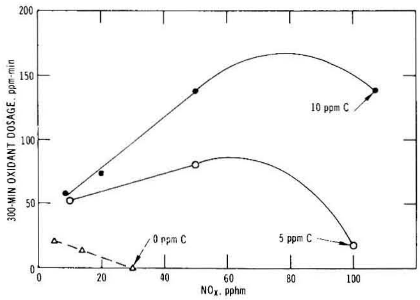

Figure 6. Effect of NO_x concentration on oxidant dosages from atmospheric hydrocarbon mixes

Table V. Oxidant Dosage (ppm × min) at Various Levels of Initial NO_x Concentration

	1 Ppm NO_x	1/2 Ppm NO_x	1/10 Ppm NO_x
10 PPm of C in atmospheric mix	138	138	58
10 Ppm of C in paraffin mix	2	24	92
5 Ppm of C in atmospheric mix	19	82	54
5 Ppm of C in paraffin mix	0	5	66

As the HC/NO_x ratio was decreased, the carbon imbalance appeared greater. Thus, in the case of paraffin (10 ppm of C) with NO_x (1 ppm) system only 34% of the carbon could be accounted for as products. In the olefin case only 39% appeared as products. For the aromatics, only 12.5% of the carbon could be accounted for as products. The mixture showed 27% of the carbon as products. In every case at the lower HC/NO_x ratio, the product yield became poorer. However, the amount of hydrocarbon reacted is larger at the lower HC/NO_x ratio. For the paraffins, at a HC/NO_x of 10, 16.4% of the HC reacted while at the HC/NO_x of 20, 14.2% reacted. In the case of olefins, at HC/NO_x of 10, 86% vs. 80% for HC/NO_x of 20. The aromatic had 64 and 57% for the 10 and 20 HC/NO_x ratios. The lower carbon balance is observed for the greater amount of reaction. It has been shown by Altshuller and co-workers (*20*) for the propylene case that as the hydrocarbon consumption increases, the amount of carbon that can be accounted for as products decreases. Altshuller and co-workers suggest that products arising from the photooxidation of hydrocarbons are being photooxidized further—i.e., formaldehyde can be photooxidized to CO and CO_2, while acetaldehyde is photooxidized to HCHO, CO, and CO_2. The PAN being an unstable compound could decompose to a product not detected with a gas chromatograph.

In Figure 7 are shown the data for the percent reacted olefin and paraffin when paraffins are replaced with aromatics. The curves with the addition of aromatics show little or no effect.

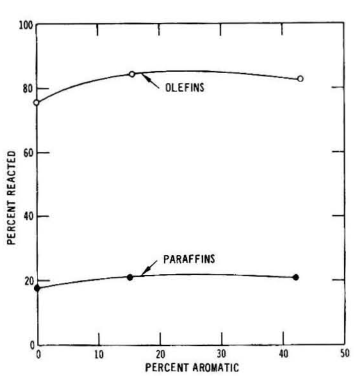

Figure 7. Percent reaction of paraffins and olefins with replacement of paraffins by aromatics in a 10-ppm C mixture with olefins kept constant at 1.5 ppm of C and NO_x at 0.5 ppm

Table VI. HC Consumed in Oxidation of NO

	40 Pphm of NO	80 Pphm of NO	HC consumed/ NO oxidized
Aromatic mix	182	292	4.1
Olefin mix	99	197	2.5
Paraffin mix	61	127	1.5
Atmospheric mix	90	190	2.3

In Table VI are shown the ratios of hydrocarbon consumed to NO oxidized. Except for the aromatics, an almost constant ratio is observed suggesting that the mechanism for hydrocarbon consumption and NO oxidation is not significantly altered during the course of the reaction. Although the stoichiometry of the chamber mixes is constant, it is approximately twice (1.4 vs. 2.3) that found in irradiated bag samples of the Los Angeles atmosphere (*7*). The lower ratio found in the Los Angeles air samples is not a result of the larger initial NO_2 concentration since the HC consumption/NO oxidized is not altered during the course of the reaction (2.25 at 40% NO oxidation vs. 2.38 with 80% NO oxidation). Apparently, other species such as aldehydes are contributing to NO oxidation in Los Angeles.

Peroxyacetyl Nitrate

The peroxyacetyl nitrate (PAN) like ozone did not form until the nitric oxide was almost entirely oxidized and NO_2 was at a maximum. Although the tables do not show the time in which PAN and O_3 maximize, in general, with the more reactive olefin–NO_x and aromatic–NO_x systems, the PAN always maximized after the ozone. The data suggest that for all systems, the PAN dosage increases with increasing NO_x concentrations. It had been reported earlier (*20*) that the PAN at constant HC but with increasing NO_x would maximize and then decrease with additional NO_x. This maximum occurs at a HC/NO_x of 6.5/1. Since most of the HC/NO_x ratios in this study were above this, the maximum was never reached. In the olefin–paraffin and the aromatic–paraffin systems, the PAN increased with increasing reactive hydrocarbon—i.e., olefin or aromatic. At 100% olefin and 100% aromatic, the PAN dosage is slightly greater for the olefins than for the aromatics. The PAN data for the individual classes are shown in Table III.

Eye Irritation Responses

The eye irritation measurements are based on intensity values of 0–5 scale. In this method, the subject rates the degree of severity of irritation after being exposed to the pollutant for a specific time. Exposure of the panel to clean air irradiated 300 min gave average response values of 0.30, 0.50, and 0.40 for three replicate runs. With air containing 1.0 ppm NO_x, the response for a single run was 0.30. Altshuller et al. (*23*) gave similar values for irradiated air in the presence of NO_x (0.2 ppm of NO_x, 0.75; 0.3 ppm of NO_x, 0.6; 1.2 ppm of NO_x, 0.5 unit). There are technical problems associated with the measurement of 0.3–0.5 unit since the subjects are usually suspicious of the potency of the particular irritant. Therefore, all values around 0.2–0.5 should be considered background levels.

The average eye irritation values for the hydrocarbon mixture is shown in Table III. A slight increase in eye irritation with HC concentration appears with all levels of NO_x studied. The lowest NO_x value—i.e., 0.1 ppm gave the intermediate eye irritation index (0.82 for 0.1 ppm of NO_x, 0.6 for 0.5 ppm of NO_x, and 1.0 for 1.0 ppm of NO_x), but the number of values obtained at this low NO_x level are few and the values may not stand up upon replication.

In the olefin–paraffin and the aromatic–paraffin mixtures, the eye irritation shows an increase with increasing olefin or aromatic. The aromatics gave the highest eye irritation index. This is probably a result of peroxybenzoyl nitrate formation from the photooxidation of aromatics (*24*).

Effect of Added CO, Benzaldehyde, and Acetaldehyde on Hydrocarbon–NO_x Mixtures

Three series of runs were made on studying the effect of added CO on NO oxidation in the absence and presence of hydrocarbons (*25*). In the absence of HC, the effect of adding CO to the time for NO_2 maximum decreased from over 300 min with no CO to approximately 135 min with the addition of 100 ppm CO at 0.5 ppm of NO. When CO was added to paraffin–NO_x system (10 ppm of C/0.5 of NO_x), the results were inconclusive since the time for NO_2 maximum averaged 200 min with no CO added while with 20 ppm of CO, the NO_2 maximum appeared at 160 min. When 100 ppm of CO was added to the paraffin mix, the time for NO_2 maximum was 165 min. For a series of runs containing paraffins, olefins, and aromatics (5 ppm of C/0.5 ppm of NO_x), the addition of CO appeared to have little effect on the NO_2 maximum. Thus, with no CO added, the NO_2 maximum occurred at about 66 min (average of several runs), with 20 ppm of CO the NO_2 maximum occurred at 54 min while with 100 ppm of CO, the NO_2 maximum occurred at 62 min. The results of this study suggest that a CO effect cannot be very great under real atmospheric conditions.

A CO effect would be expected if the CO can effectively compete with OH radicals that are present in the atmosphere. The rate constant for OH with reactive hydrocarbons is ~60 times greater than with CO. If one assumes that a typical city would have approximately 1 ppm of CO with an equal concentration of NMHC, then the reactive hydrocarbon portion of the 1 ppmC would be approximately 0.15 ppm (v/v). The CO to reactive hydrocarbon ratio is then 6.6. This is ten times less than is required to account for the difference in rate constants. Therefore, just from theoretical considerations, no CO effect should be expected.

The reactivity of the olefin mixture was tested with the addition of acetaldehyde and benzaldehyde (*26*). When 2.5 ppm (v/v) of acetaldehyde was added to olefin–NO_x mixture (10 ppm of C/1.0 ppm of NO_x), the oxidant dosage and the PAN yield increased. The time for NO_2 maximum decreased while the eye irritation level remained constant. When 2.5 ppm (v/v) of benzaldehyde was added to the olefin mix, almost every reactivity parameter except eye irritation was decreased. The level of eye irritation almost doubles with the addition of benzaldehyde.

Summary and Concluding Comments

Substituting aromatics for olefins causes a decrease in both oxidant and PAN dosages. These reactivity parameters are further decreased by replacing aromatics with paraffins. Replacement of olefins with paraffins also causes a decrease of oxidant and PAN yields.

The results of simulated atmospheric mixtures did not show a substantial eye irritation effect by substituting aromatics with olefins. A substitution of paraffins for either olefins or aromatics showed a decrease in eye irritation.

Benefits derived from NO_x controls on oxidant dosage are dependent upon the HC/NO_x ratio and types of hydrocarbons. If a polluted atmosphere contains 10-ppm C of atmospheric mix and the HC/NO_x ratio is above 14/1, then a reduction in NO_x would have a corresponding decrease in oxidant. When the ratio is above this value, control of NO_x would have little and perhaps a worsening effect on oxidant production. At 5-ppm C atmospheric mix, similar effects are observed, although the dependence of oxidant above a HC/NO_x ratio of 7/1 is less pronounced.

What was particularly interesting in this study was the oxidant arising from the photooxidation of paraffins. The data show that the oxidant dosages for the atmospheric mix and the reactivity differences between paraffins and the atmospheric mix reverses with increasing HC/NO_x ratio. The implication for the real atmosphere is that while at higher NO concentrations the removal of olefins and aromatics can be expected to reduce oxidant dosage, at lower NO concentrations the reactivity of the remaining paraffins may increase oxidant dosage, but removal of aromatics and olefins is still effective. It was noted that paraffins form very little oxidant in terms of dosage after 5 hr of irradiation. However, the slope of the O_3 vs. time curves at the close of the irradiations is very large. One can only speculate what ozone levels would result from prolonged irradiations. One can also wonder what happens when a "spent" air mass is irradiated further—i.e., under conditions where only the saturated hydrocarbons remain and are being transported downwind with low NO_x levels (high HC/NO_x ratios). Can significant quantities of oxidant arise? These chamber studies suggest that oxidant should be produced under these conditions. Field studies measuring actual atmospheric conditions are needed to verify this hypothesis.

It must be emphasized that the reactivity parameters obtained in this study are for the conditions previously described and any conclusions that are derived must be considered in light of these experimental conditions.

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Received for review September 30, 1974. Accepted January 27, 1975.

Rapid Formation of Iminodiacetate from Photochemical Degradation of Fe(III)nitrilotriacetate Solutions

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■ Gas chromatography has been used to monitor the rapid photodegradation which dilute solutions of Fe(III)–nitrilotriacetate undergo when exposed to sunlight. Iminodiacetate is produced in essentially stoichiometric amounts and is only very slowly photodegraded to glycine under the same conditions. The resulting accumulation of iminodiacetate in natural water systems with continuing input of nitrilotriacetate, which these observations suggest, is of environmental concern because of the possible carcinogenic activity of *N*-nitroso iminodiacetic acid.

The ferric nitrilotriacetate (NTA) complex has been reported to be sensitive to photodegradation (*1*). The main nitrogen-containing compound found after irradiating a $10^{-2}M$ Fe(III)–NTA solution was identified as iminodiacetate (IDA) by comparing melting points of derivatives of the acid insoluble material with those of an authentic sample of IDA.

This observation of the abiotic formation of IDA from NTA is of considerable importance. The formation of IDA from the bacterial degradation of NTA has been postulated (*2*), but numerous workers have been unable to detect any experimentally (*3–5*). The possibility of forming the secondary amine, IDA, and its presumably carcinogenic nitrosation product has been one argument against the large-scale use of NTA as a detergent builder.

The recent development of sensitive direct methods for the determination of NTA (*6*) and IDA in environmental water samples without interference from other aminopolycarboxylic acids or metal cations has made possible the quantitative study of this system presented here. The results show a rapid photodegradation of ferric NTA in sunlight to give IDA and a relatively slow photodegradation of IDA to glycine under similar conditions. The possibility of accumulation of IDA in a water system with a constant input of NTA is therefore suggested.

Experimental

NTA was determined as its trimethylsilyl (TMS) ester using a gas chromatographic method described elsewhere (*6*). The method is based on the addition of excess EDTA to the aqueous sample to scavenge metal ions, releasing NTA and other aminocarboxylic acids from their metal complexes before evaporation to dryness and derivatization. The trimethylsilyl ester is formed by reaction with bis(trimethylsilyl)trifluoroacetamide in dimethylformamide at 70°C. Temperature-programmed gas chromatography on a 6 ft × ⅛ in. o.d. stainless steel column packed with 5% OV-17 on chromosorb W–HP using *n*-octadecane as internal standard gave good separation from other peaks. A Perkin-Elmer Model 990 dual column gas chromatograph with flame ionization detection was used.

Test solutions were analyzed for IDA and glycine using a similar procedure, but on a different column. A persistent, unidentified peak with retention characteristics very similar to the IDA–TMS derivative was observed on the 5% OV-17 column used for NTA analysis when analyzing samples known to contain no IDA. A 6 ft × ⅛ in. o.d. 7% SE-30 on Chromosorb W–HP stainless steel column gave no positive interference for IDA, and glycine and was successfully used for analysis of solutions containing small amounts of these compounds. On-column losses on the order of 10 ng of glycine, IDA, and NTA were observed with this column even after periods of extensive conditioning and continuous use, precluding its use for derivatized samples containing less than approximately 10 ng μl^{-1} in the final silylation mixture.

A stock solution of $10^{-2}M$ Fe(III)–NTA was made by dissolving 1.37 grams of Na_3–NTA·H_2O and 1.35 grams of $FeCl_3 \cdot 6H_2O$ in water, adjusting the pH to 4.4 with sodium hydroxide, and diluting to 500 ml. The slight precipitate which formed initially dissolved on standing overnight. Working solutions of $10^{-3}M$ Fe(III)–NTA were made by dilution when needed. The pH of the $10^{-3}M$ Fe(III)–NTA solution was 5.2. Test solutions were divided into two equal 100-ml portions. One was placed on the roof of a building at MIT (latitude approximately 42° 20′ N) in a rubber-stoppered borosilicate flask. The other was placed in a dark cabinet.

The bulk of the experiments were done in late July, and reported exposure times include periods of night. In general, the weather was sunny and hot (approximately 25–30°C) throughout the test period, although there were some overcast days during the long-term experiment. Samples (6 ml) were taken at intervals as noted in the various figures, and subsamples of 1.00 and 0.10 ml were taken for IDA and glycine analysis and for NTA analysis, respectively. The remainder of each sample was used for pH measurement. Evaporation of the samples was initiated promptly after each sample was taken. All dried samples were stored in the dark for the time prior to analysis.

A stock solution of $10^{-2}M$ Fe(III)–IDA was prepared by dissolving 0.66 gram of IDA as the acid and 1.35 grams of $FeCl_3 \cdot 6H_2O$ in water and diluting to 500 ml. Working solutions of $10^{-3}M$ Fe(III)–IDA were prepared by dilution, and the pH was adjusted to 2.6 with sodium hydroxide solution. The pH could be raised no higher without precipitation of the iron. The Fe(III)–IDA mixtures were prepared and exposed to sunlight under conditions essentially the same as those in the NTA degradation studies.

Solutions of NTA with other metals were made by weighing out an amount of the metal chloride equivalent on a molar basis to 40 mg of NTA and dissolving it in approximately 50 ml of water. An aliquot of 1.000 ml of 1000 ppm NTA stock solution (slightly ammoniacal) was added together with water to give a final volume of 100.0 ml. Aliquots of these 10-ppm NTA solutions containing a forty-fold molar excess of Cd^{2+}, Cu^{2+}, Pb^{2+} or Cr^{3+} were analyzed for NTA, and the remaining solution was exposed to the sun for a week. Aliquots were then taken, treated with EDTA, evaporated, and stored in darkness until derivatized for analysis.

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Results and Discussion

Within 1.5 hr, a slight gelatinous orange precipitate was observed in the Fe(III)–NTA solutions exposed to sunlight. The volume of this precipitate increased throughout most of the first day. As seen in Figure 1, the concentration of NTA decreased rapidly over a period of 9 hr, and the concentration of IDA increased correspondingly. Under the conditions of our experiment, the decay of the NTA concentration over the first 9 hr was exponential and the plot of concentration on a log scale vs. time was linear with an approximately 1.5-hr half-life. After going through a maximum, the concentration of IDA decreased slowly by about 35% over the 7-day exposure period (Figure 2). Meanwhile the concentration of glycine present increased as the IDA decreased, the sum of the two remaining approximately constant (within 10%) after the first 24 hr. The control samples kept in the dark showed no signs of pH change, precipitate formation, loss of NTA, or formation of IDA over a period of at least a week.

Published results (*1*) indicated that the efficiency of photodegradation, and therefore the rate under constant illumination, is a function of pH, slower rates being expected at higher pH. A comparison of the rates of photodegradation of Fe(III)–NTA at pH 5.2 and 7.0 was planned, but at both pH values, the residual NTA concentration was indistinguishable from zero after one day. On continuing exposure, slow degradation of the IDA was observed, 67% of the stoichiometric amount still remaining after 2 weeks at pH 7.0 and 45% at pH 5.2. Exposure of a millimolar Fe(III)–IDA solution at pH 2.3 showed more rapid degradation and corresponding formation of glycine (Figure 3). Photodegradation of glycine, if it takes place at all under the conditions of our experiments, is very much slower than that of NTA or IDA.

Solutions containing 10 ppm of NTA in a 40-fold excess of a metal ion (Cd^{2+}, Cu^{2+}, Pb^{2+}, or Cr^{3+}) were exposed to sunlight for a week and analyzed for residual NTA. After exposure, no significant change was found for Pb^{2+} and Cd^{2+}, a marginally significant decrease for Cr^{3+} and a marked (70%) decrease for Cu^{2+}. Thus it appears that Cu^{2+} is also a photosensitizing agent for NTA. Since the completion of this work, a study of the photooxidation of Cu(II)–NTA complexes has been reported (*7*).

The significance of these findings with respect to the fate of NTA in natural water systems depends on whether photosensitive complexes of NTA and its degradation products actually are formed in significant amounts. Prediction of the speciation of low concentrations of NTA in natural water systems is difficult and complicated because of the variability of their composition, the large number of possible reactions, and the uncertainties in their equilibrium constants and rates. For each natural water system, calculations must be made on the basis of a model involving many assumptions and approximations. Nevertheless, some conclusions are fairly clear. Equilibrium calculations on a model of Lake Ontario (*8*) assuming total copper present to be $2 \times 10^{-6}M$ indicated that between 23 and 36% of the total NTA at the $3 \times 10^{-6}M$ level would be bound as ferric complexes and the bulk of the remainder as the copper complex over the pH range 6–9. An elaborate mathematical model of a natural water system involving 21 metals and 32 ligands led to the conclusion that at pH 8, NTA present at a total concentration of only $10^{-7}M$ would hold more ferric ion in solution as a complex than would any inorganic ligand (by five orders of magnitude) and more than any low-molecular-weight organic ligand likely to be present other than citrate (*9*). The predominant NTA species from this model would be expected to be complexes of copper, nickel (if present), magnesium, calcium, zinc, lead, and iron. The total concentrations of copper, lead, nickel, and zinc assumed for the model were relatively high for a natural water system, which would suggest that in most natural waters, the iron complexes would be of greater importance than the calculations indicated. The ultimate distribution of NTA in any system will be a function of the concentra-

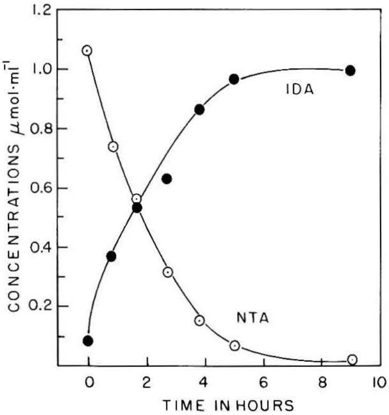

Figure 1. Rapid photodegradation of $10^{-3}M$ Fe(III) NTA in sunlight with production of IDA at pH 5.2–5.8

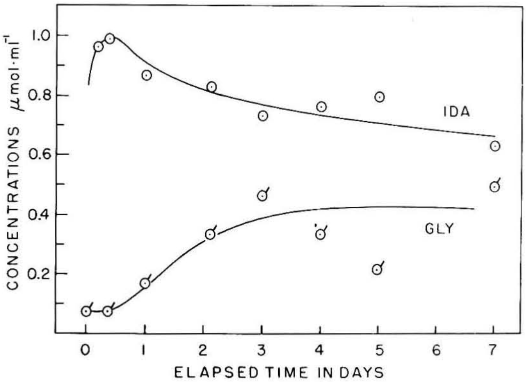

Figure 2. Photodegradation of IDA in sunlight with production of glycine at pH 5.8

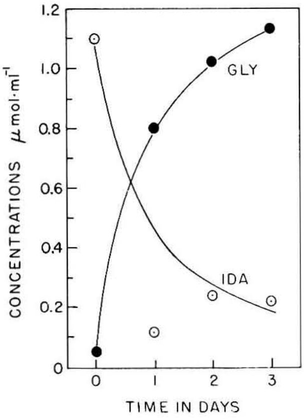

Figure 3. Rapid photodegradation of $10^{-3}M$ Fe(III) IDA in sunlight with production of glycine at pH 2.3

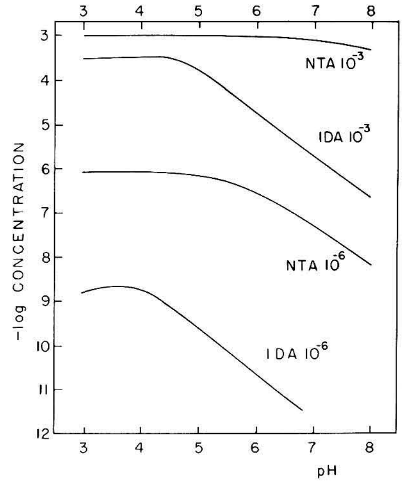

Figure 4. Concentration of Fe(III) NTA complex and Fe(III) IDA complex in equimolar mixtures of metal and ligand as a function of pH

tion of the NTA itself, the various metals, their stability constants, the availability of competing ligands, and the pH.

The photodecomposition of Fe(III)–NTA produces Fe(II), formaldehyde, and CO_2 as well as IDA (*1*). Oxygen from the air readily reoxidizes Fe(II), whether as NTA complexes, IDA complexes or free ferrous ion over the pH range in question, so Fe(III) is replenished to continue the reaction. The Fe(III)–NTA complex stability constant is very large and therefore Fe(III) competes effectively with other metal ions for available NTA even though the concentration is low. Most metal NTA complexes undergo exchange readily, and this kinetic factor is favorable to the formation of Fe(III)–NTA and the photodecomposition process.

The very much slower rate of photodecomposition of the Fe(III)–IDA complex when compared with the NTA complex in the pH range 5–7, is probably the result of the much lower stability constant of the IDA complex. By use of the data from the literature (*10, 11*) to calculate the conditional stability constants (which correct for competing reactions such as the hydrolysis of the metal ion and the protonation of the ligands), it was found that the constant for the NTA complex was between 4 and 5 powers of 10 larger than that of the IDA complex over the pH range 3–8. From these constants, and by assuming equal concentrations of Fe(III) and total ligand, the equilibrium concentrations of the complexes have been calculated as a function of pH for $10^{-3}M$ and $10^{-6}M$ solutions. The results, summarized in Figure 4, show that although the NTA complex at millimolar concentrations is never more than 8% dissociated over the entire range of pH 3–8, the IDA complex is 50% dissociated at pH 3, 80% at pH 5, and over 99% dissociated above pH 6.5. At lower total concentrations of metal and ligand, such as $10^{-6}M$, the IDA complex is essentially not formed at all, although the NTA complex is less than 50% dissociated below pH 6. These conclusions agree with the observation that photodegradation of Fe(III) complex at pH 5–6 resulted in precipitation of hydrous ferric oxide and accumulation of IDA in solution.

Although investigators working on bacterial degradation have been unable to isolate any intermediates of NTA degradation external to the cell itself, it must now be recognized that the photodegradation of NTA as the iron complex provides a rapid mechanism for the formation of IDA, but that the IDA formed is relatively resistant to further photodegradation at the pH of most natural waters.

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Received for review June 10, 1974. Accepted January 23, 1975. This work was supported in part by the United States National Science Foundation under Grant GP33950.

Characterization of Australian Crudes and Condensates by Gas Chromatographic Analysis

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During the past decade, the growth in the international movement of crude oil by the sea route, has led to a marked increase in the number of instances of pollution of the marine environment. Consequently, there is a need for rapid and accurate identification of the pollution source for the control and policing of this form of environmental contamination.

Various methods have been suggested for identifying the source of crude oil slicks—e.g., infrared spectroscopy (*1–4*), ultraviolet fluorescence spectroscopy (*5, 6*), trace elemental analysis by atomic absorption (*7–9*), neutron activation analysis (*10*), and mass spectrometry (*11*). However, at this stage, gas chromatographic analysis appears to be the most rapid and effective of the instrumental techniques employed in the "fingerprinting" of crude oil (*4, 12–16*).

■ Development of present gas chromatographic techniques has yielded a viable means of characterizing crude oil and condensate samples for subsequent application to the source identification of oil pollution and the delineation of geological formations. Differing from previously documented fingerprint methods, this technique utilizes only that portion of crude petroleum boiling between 232°C (450°F) and 316°C (600°F), rather than examination of the total crude sample. From the gas chromatographic profile of this fraction a number of easily quantifiable parameters, involving the ratio of *n*-paraffin and isoterpenoid components, may be determined. This facilitates rapid differentiation between crude samples from separate sources. By this method a number of Australian crudes and condensates have been characterized. In addition, this technique has been demonstrated to be directly applicable to the identification of the origin of marine pollution.

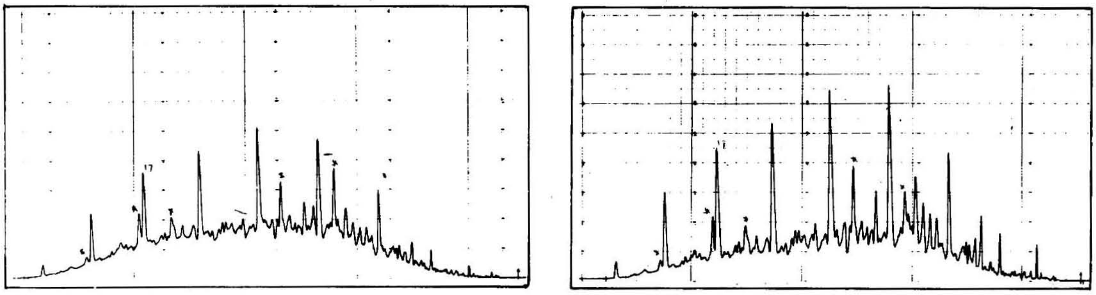
In this method, the chromatogram profiles of the crude oil samples are used as the basis for differentiation, since variations in the hydrocarbon composition of crude oils may be readily observable as alterations in peak configuration and size. If we assume that sampling of the pollutant is not difficult, the only major problem of this method is the loss of a large portion of the crude as a result of evaporation, dissolution, microbial decomposition, and chemical attack. Consequently, analysis of a fresh sample of crude and the same crude after weathering may yield two quite different chromatogram profiles.

This problem has been overcome to some degree by the use of compositional parameters as suggested by Kreider (*15*), and Ehrhardt and Blumer (*16*). Their characterization is based on two reference component pairs—*n*-heptadecane–pristane and *n*-octadecane–phytane. However, due to the low concentration of these compounds in the whole crude sample, extremely sensitive analysis and resolution are necessary to derive a meaningful parameter. In addition, by analyzing a whole crude sample, little detail is shown of the other peaks present—e.g., alicyclics and aromatics, of even lower concentration. Consequently, in an attempt to improve the accuracy of this method of characterization we have concentrated the parameter components by analyzing only a portion of the total crude sample, and we have increased the number of points of reference used for characterization.

In the present study the range of sample examined is restricted to the C_{12} to C_{20} hydrocarbons present in each particular crude or condensate. This is achieved by analysis of only that portion of crude boiling in the temperature range of 232°C (450°F) to 316°C (600°F)—the middle distillate fraction—incorporating the isoterpenoid compounds employed by Ehrhardt and Blumer (*16*) as the basis of their technique. In addition to concentrating these isoterpenoid components, selection of this cut enables observation of previously unresolved peaks, thereby broadening the basis of comparison of one crude to another. Moreover, utilization of this fraction almost eliminates any error introduced by weathering of a sample and subsequent loss of the lighter, more volatile components.

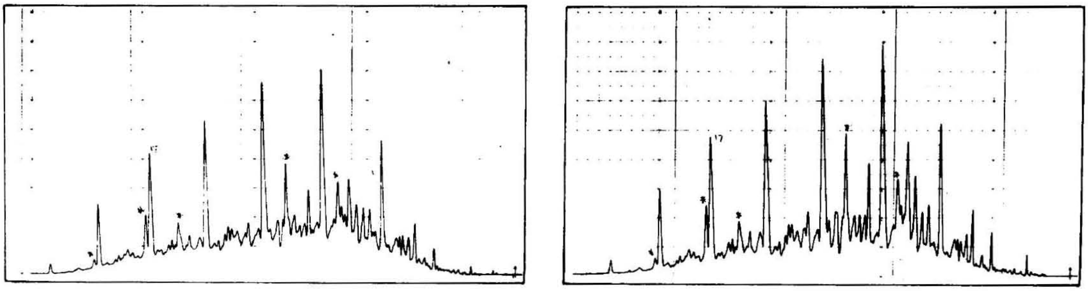
Attention has been drawn to the fact that the presence of the isoterpenoid class of hydrocarbons in crude oil is indicative of the biogenic origin of petroleum, since they are the probable derivatives of the systematic degradation of constituents of living organisms (*17–19*). As the composition of each crude is dependent on the source materials and the history of its formation with respect to temperature, pressure, and time, so the isoterpenoid composition of crude will vary from one source bed to another.

Thus, because of the detailed nature of the chromatogram profile of the middle distillate cut, it is our belief that in addition to being a marine pollution identificant, this method will be of considerable use in differentiating



a) Rankin 1 Crude

b) Nth Rankin 2 Condensate



c) Nth Rankin 4 Condensate

d) Angel 2 Condensate

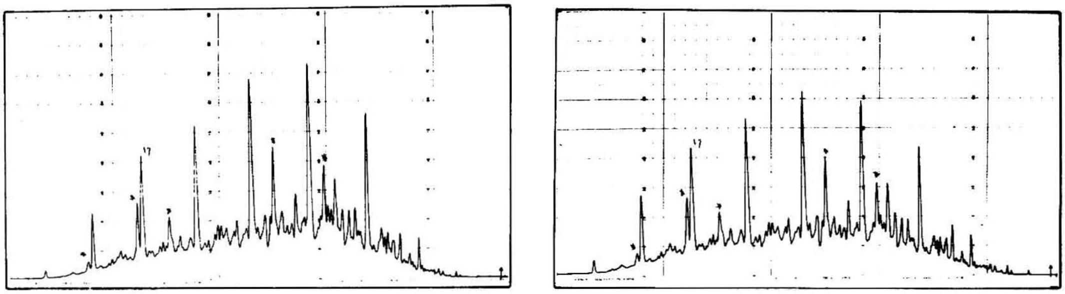
Figure 1

between closely related source beds, either in adjacent structures or at different levels of the same well, thereby aiding geologists in delineating the extent of a particular hydrocarbon source.

Experimental

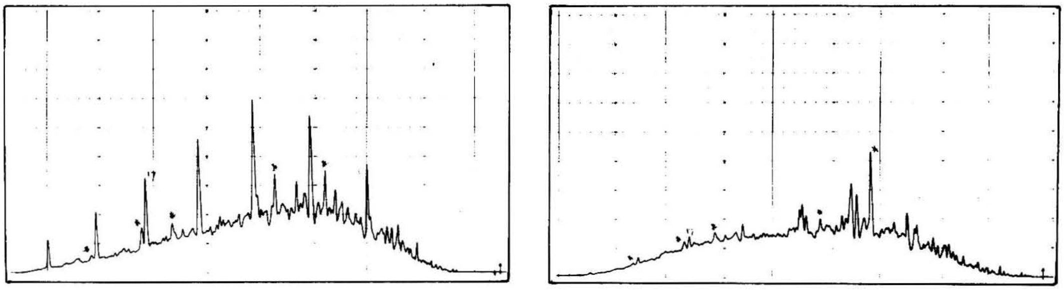
Fractionation of the various crudes and condensates was performed under a 10-mm Hg vacuum in a Sarnia 15-5 distillation unit, according to the tentative method for the distillation of crude petroleum using a 15-theoretical-plate column—ASTM D2892/71T.

The distillation cuts were analyzed on a Perkin-Elmer F30, F.I.D. gas chromatograph, using a 10-meter, 0.01-in. internal diameter, stainless steel, capillary column, coated with OV-101 silicone. Using helium at a pressure of 15 psi as a carrier gas, a 40 to 1 stream splitter was employed for



a) Goodwyn 3 Condensate

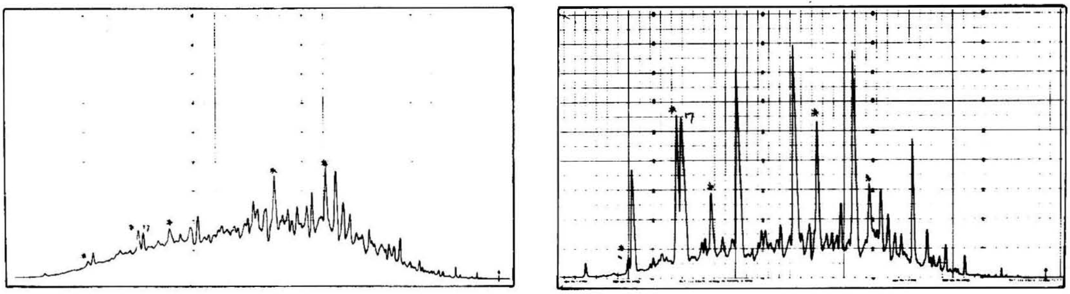
b) Goodwyn 3 Crude



c) Egret 1 Crude

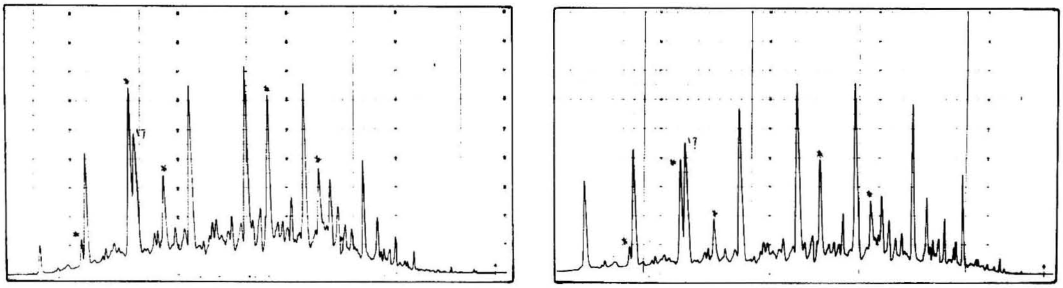
d) Eaglehawk 1 Crude

Figure 2



a) Barrow Island Crude

b) Kingfish Crude



c) Halibut Crude

d) Mackerel Crude

Figure 3

Table I. Compositional Parameters of Australian Crudes and Condensates

Sample	Location	Crude–condensate	n-C_{14}/iso	n-C_{15}/iso	n-C_{16}/iso	n-C_{17}/iso	n-C_{18}/iso
Rankin 1	North-West Shelf	Crude	1.26	1.55	2.06	1.61	2.92
Nth Rankin 2		Condensate	2.20	1.69	2.84	2.03	4.35
Nth Rankin 4		Condensate	2.20	1.72	2.87	2.00	4.39
Angel 2		Condensate	2.37	1.51	3.17	1.96	4.76
Goodwyn 3		Condensate	1.90	1.52	2.43	1.62	3.66
Goodwyn 3	Dampier Sub-Basin	Crude	1.88	1.54	2.44	1.63	3.58
Egret 1		Crude	1.55	1.75	2.71	2.10	3.50
Eaglehawk 1		Crude	0.66	1.11	1.19	1.15	1.43
Barrow Island	Carnarvon Basin	Crude	0.78	0.76	1.25	0.95	1.48
Kingfish	Gippsland Basin	Crude	2.42	1.50	2.53	0.99	5.13
Halibut		Crude	1.78	1.23	1.99	0.77	3.22
Mackerel		Crude	2.61	1.66	2.98	1.14	4.55
Moonie	Surat Basin	Crude	1.45	1.31	2.41	1.31	4.20
Mereenie	Amadeus Basin	Crude	4.11	2.65	3.49	3.53	3.37
Tirrawarra	Cooper Basin	Crude	2.70	1.51	2.69	1.12	4.38

sample introduction. The initial temperature of analysis was 50°C, rising at 2°C/min to 150°C, by which time all components had eluted. Fifteen Australian crudes/condensates were analyzed. Typical examples of the chromatogram profiles are shown in Figures 1–3.

Peaks varying most in size from one sample to another are those attributed to isoterpenoid hydrocarbons and are labeled with an asterisk. These peaks have been assumed to be [after Calvin et al. (*20*)], in order of boiling point: 2,6,10-trimethyl dodecane (farnesane); 2,6,10-trimethyl tridecane; 2,6,10-trimethyl pentadecane; 2,6,10,14-tetramethyl pentadecane (pristane); and 2,6,10,14-tetramethyl hexadecane (phytane). Confirmation of the identity of these peaks is presently being undertaken by combined GC-MS analysis.

The compositional parameters used as basis for characterization [in a similar manner to Ehrhardt and Blumer (*16*)] were the ratios of the adjacent peaks: *n*-tetradecane–farnesane; *n*-pentadecane–2,6,10-trimethyl tridecane; *n*-hexadecane–2,6,10-trimethyl pentadecane; *n*-heptadecane–pristane; and *n*-octadecane–phytane. These ratios, calculated directly from peak heights above the baseline, are given for each Australian crude/condensate in Table I, using the general nomenclature of n-C_i/iso for the above ratios.

Results and Discussion

As may be observed, the compositional parameters vary considerably from one sample to another, thus satisfying the first criterion of any identification technique of allowing a rapid and accurate differentiation between samples. In the particular case of distinguishing between samples from adjacent wells over similar structures, analysis of samples from Woodside-Burmah's North-West Shelf leases has resulted in the following observations.

Chromatogram profiles of the two North Rankin condensates (obtained from wells 3 miles apart), appear essentially identical, so it may be assumed that these condensates are enclosed in the same geological formation. However, the compositional parameters of the Egret 1 crude and Angel 2 condensate (14 and 35 miles northeast, respectively, from the North Rankin structure) are both quite different from those of the above samples, indicating that these two hydrocarbons have originated from different source beds than the North Rankin condensates.

Moreover, compared to the condensates, the Egret crude exhibits a lessening in *n*-paraffinic character with respect to the aromatic/alicyclic background, a feature also observable in the profile of the Rankin 1 crude from a site some 49 miles to the southwest. However, reference to the respective parameters allows differentiation between the two crudes.

Eaglehawk crude provides a striking example of the varying nature of petroleum. Located only some 10 miles northeast of the North Rankin structure, and 5 miles west of the Egret field, this crude is almost totally devoid of *n*-paraffins in the region examined [Figure 2(d)]. In this regard it is similar to Barrow Island crude (100 miles to the southwest) [Figure 3(a)], yet once again identification may be made by use of the characteristic ratios.

By use of the parameters, comparison may also be made between hydrocarbon samples located at different levels of the same well—e.g., the Goodwyn 3 condensate and crude, where the interval over which the crude was detected lies some 400 ft below that of the condensate. The respective chromatogram profiles appear identical, and excellent agreement between the parameters is observed, indicating that both samples originate from the same source bed. Moreover, this may indicate that a link exists between the two hydrocarbon-bearing sand zones at the different levels.

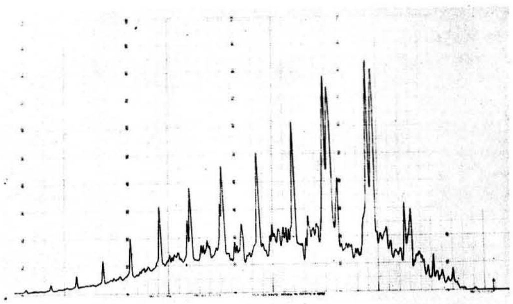
Gippsland Basin crudes from the neighboring Kingfish, Halibut, and Mackerel formations, and the on-shore crudes of the Moonie, Mereenie, and Tirrawarra fields, all exhibit marked variation in character, and all are individually characterized by their respective parameters.

Practical Application

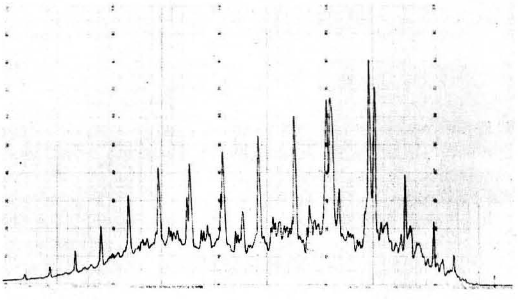
The application of this characterization technique to actual pollutant samples has also been demonstrated. In four separate instances of oil pollution in Australian waters, this laboratory has successfully identified the source by use of this method. For example, a slick consisting of approximately 100 gal of heavy fuel oil was observed in Cairns Harbour in November of last year. Samples of the pollutant and a fuel oil from the suspected source were collected and forwarded to this laboratory for analysis.

Separation of entrained water and solids from the pollutant was performed according to the method of the Federal Water Pollution Administration (*21*). Subsequently both the pollutant and fuel oil sample were fractionated under a 1-mm Hg vacuum in a specially designed microdistillation apparatus, to collect the 232–316°C (450–600°F) "fingerprint" cut. Total sample charged was approximately 25 ml; fraction collected was less than 5 ml.

Fingerprints were then obtained of the two fractions



a) Fingerprint of Pollutant.



b) Fingerprint of Suspect Fuel Oil.

Figure 4

Table II. Parameter Correlation of Pollutant/Source Hydrocarbons

Parameter	Bunker fuel oil	Spill fuel oil
n-C_{14}/iso	1.79	1.93
n-C_{15}/iso	2.13	2.20
n-C_{16}/iso	2.01	2.00
n-C_{17}/iso	1.44	1.43
n-C_{18}/iso	1.36	1.40
Ni/V	0.068	0.067

(Figure 4) and characterization parameters determined (Table II). Excellent overall correlation is observed between the two sets of data, although slight variation is noticeable in the parameters involving the lowest boiling components. This variation is consistent with preferential evaporation of the more volatile component of the parameter pair of the pollutant sample. For example, n-C_{14} boiling point is 252°C (488°F), farnesane boils at 246°C (475°F), therefore the n-C_{14}-farnesane ratio increases with exposure to weathering. Consequently n-C_{14}-farnesane (pollutant) will be greater than n-C_{14}-farnesane (original fuel oil), as is observed.

Such data were produced as evidence in the subsequent prosecution of the offender, and largely as a result of the "fingerprint" data, the defendant was found guilty and a $10,000 fine, plus costs, was imposed.

Acknowledgment

The authors wish to express their thanks to Burmah Oil Co. (Australia) for providing hydrocarbon samples from the North-West Shelf and for allowing publication of the material reported here.

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Received for review September 5, 1974. Accepted February 7, 1975.

Iodate Formation and Decomposition in Iodometric Analysis of Ozone

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The absorption of gaseous ozone in neutral buffered potassium iodide solutions is the basis of a standard analysis used to measure ozone concentrations ranging from 0.01 ppm to many percent. However, much controversy has emerged regarding the stoichiometry of the method. A number of investigators have studied this analysis at intermediate concentrations (IC, 1–100 ppm), and high concentrations (HC, 100–10^4 ppm) where the ozone concentration and liberated iodine were measured directly. Apparently, the stoichiometry of the analysis at low concentrations (LC, 0.01–1 ppm) has been standardized only by dilution of ozone streams that were themselves analyzed at IC or HC.

The accuracy at LC is of great practical interest because it is the basis of a reference method adopted by the Environmental Protection Agency (*1*). The accuracy at HC is significant because many investigations at IC and LC, in-

■ The absorption of high ozone concentrations (1500–6000 ppm) using glass frits in "neutral" buffered KI produces a second substance, S, in addition to iodine. In both "neutral" buffered and more acidic solutions, both S and iodate react to form iodine according to

$$C/C_0 = \exp\{-2.08(\pm 0.45) \times 10^{11} [H^+]^2\}t$$

(where $[H^+]$ is given in moles/liter and t is in hours). Thus it is concluded that S is iodate in agreement with a previous polarographic identification of S formed at lower concentrations. This possible formation and spontaneous decomposition of S with time should be considered in ozone analyses.

cluding the original work on which the Federal method is based (*2*), were standardized by titrimetric analysis of undiluted streams at HC. HC analysis is also of importance in its own right for the monitoring of emissions sources, such as ozonation plants, and for chemical investitions.

Birdsall et al. (*3*) and Byers and Saltzman (*2*) have reviewed studies of iodometric ozone analysis dating back to 1911. Additional investigations have been reported by Ingols et al. (*4*), Boyd et al. (*5*), Hodgeson et al. (*6*), Kopczynski and Bufalini (*7*), Parry and Hern (*8*), and Dietz et al. (*9*). In general, there has been much controversy regarding the stoichiometry of these analyses. The disagreement between numerous and apparently well-executed scientific studies is perplexing.

We investigated the absorption of 1000–10,000 ppm of ozone in neutral and near-neutral buffered iodide solutions (HC). This study revealed a new effect which may partially account for the discrepancy between previous investigations at HC and provides additional evidence of the iodate formation suggested by Kolthoff and Belcher (*10*) and reported by Parry and Hern (*8*).

Effects of Absorption Parameters

To show incisively the relationship between the present experiment and previous studies, we briefly review the effects of three significant experimental variables: concentration of the ozone stream, elapsed time between sampling and analysis, and use of impingers vs. fritted glass bubblers.

While there have been indications that under some conditions the stoichiometry of absorption may vary with concentration level, in much of the literature, this is not explicitly considered. Byers and Saltzman (*2*), using midget impingers, found that IC analyses in the neutral buffered reagent give low results as compared with HC. The studies of both Byers and Saltzman (*2*) and Saltzman and Gilbert (*10*) imply that LC and IC analyses, as compared by dilution, are interconsistent. The present work, in agreement with Parry and Hern (*8*), suggests that the IC and HC analyses can give low results.

Saltzman and Gilbert (*11*) reported that the color of the iodide/iodine solution continues to intensify for about 45 min after sampling at IC is complete. They attribute this to the formation of two products when ozone is absorbed into the neutral buffered reagent. The color fades after longer times (*12*). Yet, the EPA procedure for LC (*1*), specifies that colorimetry is to be performed immediately after collection. Many reports in the literature do not state the elapsed time used between collection and analyses.

Jacobs (*13*) reports that fritted glass absorbers may give less iodine during collection than impingers. Byers and Saltzman (*2*) also suggest that the type of impinger or bubbler may influence the stoichiometry. Hendricks and Larsen (*14*) confirm this and imply that surface losses are the cause. The work of Saltzman and Gilbert (*11*) considered in light of a recent report (*8*) seems to imply that higher results can be expected from impingers.

Parry and Hern (*8*) reported that in addition to iodine, large amounts of a second product (S) are formed when 100–400 ppm of ozone are absorbed in buffered iodide using a fritted glass sparging tube. The half-wave polarographic potential of the unknown was identical to that of a blank to which iodate had been added; thus they concluded S was iodate.

Schmitz (*15*) has pointed out that if iodate is formed by either of the two possible pathways:

$$3O_3 + I^- = 3O_2 + IO_3^- \quad (1)$$

$$5O_3 + I_2 + H_2O = 5O_2 + 2IO_3^- + 2H^+ \quad (2)$$

then if the solution is acidified just before iodide determination, the reaction

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O \quad (3)$$

takes place and the overall stoichiometry of ozone to iodine conversion is identical to the classical direct reaction

$$O_3 + 2I^- + 2H^+ = I_2 + H_2O + O_2 \quad (4)$$

Experimental

In our HC investigations of ozone formation in corona discharges (to be reported elsewhere), we have tried several variations of the potassium iodide method. Extra coarse fritted glass sparging tubes (Pyrex No. 39533) were used for all of the absorptions reported here.

A neutral buffered reagent ($0.2M$ KI, $0.1M$ KH_2PO_4, $0.1M$ Na_2HPO_4) was used to absorb ozone. When the liberated iodine was first analyzed with $0.1M$ sodium thiosulfate, scattered results were obtained in replicate absorptions. However, if after ozone was absorbed and before titration, the solution was acidified with acid from a dropper bottle to overcome the buffer (approximately 2 ml of concentrated HCl was added to a 100-ml aliquot), the results were repeatable. Additional iodine was generally liberated in the acidification step. In agreement with Parry and Hern (*8*), we tentatively attributed this to the acid decomposition of a second product (S) formed during ozone absorption. The pH of this "neutral" buffered absorbent solution was 6.62 (±0.05) at 23°C. This pH was reproducible in later experiments.

When the acidified, titrated aliquots were set aside, they turned noticeably yellow after 5–10 min indicating the formation of more iodine. This process was accelerated if excessive HCl was added. Under the experimental conditions, very little additional iodine was so formed (less than 1% of the total iodine assay). This can be attributed to the oxidation of iodide (*16*):

$$4I^- + O_2 + 4H^+ = 2I_2 + 2H_2O \quad (5)$$

There was never any measurable oxidation of the unacidified, buffered iodide solution which at times was stored for a month or more.

We were also concerned lest larger amounts of iodine might somehow be formed when the acidified solutions were allowed to stand before titration. We believed that S was iodate. Therefore, to systematically examine the above possibility, we prepared solutions of the absorbent containing iodate. Here again, the increase in iodine titer, 10 min after acidification, was small.

However, during this experiment, it was noticed that the *unacidified* neutral buffered KI/KIO_3 stock solution turned noticeably yellow over a long period of time. After a week, most of the iodate in the solution had reacted to form iodine. We subsequently confirmed that S would also spontaneously form iodine in the neutral buffered absorbent.

Because of this unexpected result, we decided to see whether the iodate reaction also occurred in a truly neutral solution. An unbuffered solution consisting of 20 ml of $0.1M$ KIO_3 and 980 ml of $0.2M$ KI was prepared using distilled water and the pH was adjusted to 7.1 (±0.1) with sodium carbonate. After two weeks, less than 0.5% of the iodate had reacted to form iodine. Similar results were obtained in more basic solutions.

To quantify the reaction rates of S and iodate to form iodine as a function of pH, 20 ml of $0.1N$ KIO_3 solution was made up to a liter with KI ($0.2M$) and solutions of MacIlvaine's buffer (*17*). S was prepared by absorbing ozone from the corona discharge into similarly buffered KI solutions of different pH values. The resulting solutions, which then contained I^-, I_2, and S, or IO_3^- were set aside in glass-stoppered flasks. Aliquots (100 ml) of the solutions were periodically titrated with $0.1N$ sodium thiosulfate. After the initial titration, each sample was acidified with 2 ml of concentrated HCl and the additional iodine that was liberated was then quickly titrated. The difference between these two measurements was taken as the number of equivalents of iodate or of S remaining in the solution.

Results

At pH 5.97 and 6.27 (±0.05), significantly less S was produced by the absorption of ozone than at pH 6.62. While no general attempt was made to systematically repeat the absorptions using identical ozone stream concentrations with the several reagents, we feel the decrease in the relative concentrations of S with pH shown by the limited data in Table I represents the general trend. Because less S was formed in the more acidic solutions, the results for ozone at pH 5.97 and 6.27 were less accurate than those from the other experiments. The iodate experiments lasted from 5.7–280 hr (depending on pH and sampling frequency); those for S varied from 5.7–238 hr. The reported pH values were those at the onset of the decomposition experiments. pH was also measured at the end of a number of trials. There was a tendency for the pH to increase approximately 0.05 unit; however, this is within experimental error.

Sometimes the total iodine (initial iodine + S) decreased slightly from measurement to measurement. The cumulative loss was never more than 5% of the total. The solutions were kept in stoppered volumetric flasks, and it is felt that this loss was due to volatilization when the flasks were opened. Another possibility is that the losses were caused by iodine absorption from dust contamination (*11*) or to slow side reactions.

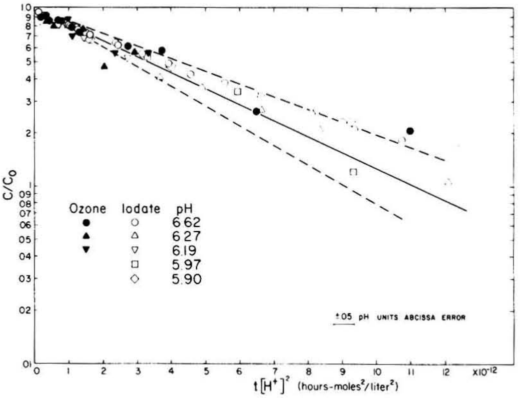

Figure 1. Concentration of S or iodate (divided by initial concentration, C/C_0) as a function of time

The abcissa variable $[H^+]^2t$ brings together the curves for various conditions according to Equation 6. Light data points are for iodate solutions, dark points represent S (see text)

Table I. Production of S vs. pH

Ozonated oxygen streams were absorbed in 500 ml of buffered $0.2M$ KI for 15—20 min

	Equivalents S		
pH	Equivalents $[S + \frac{1}{2}I_2]$	Ozone concn, ppmv	Gas flow rate, mol/min
6.62	0.22	1780	0.102
6.27	0.12	1780	0.102
6.62	0.26	6150	0.020
6.27	0.08	6150	0.020
5.97	0.06	1600	0.040

The pH buffered iodide solutions (without iodate) used during the experiments were stable during storage periods longer than the duration of the experiments; iodide oxidation was never noticeable in any of the unacidified reagents.

Data are shown in Figure 1. In all instances, a first-order rate of decomposition was observed. The rate was, within experimental error, proportional to $[H^+]^2$ for the pH range investigated (5.97–6.62). These data are consistent with the rate equation

$$\frac{d[C]}{dt} = -2.08(\pm 0.45) \times 10^{11} [C][H^+]^2 \qquad (6)$$

where C is the concentration (mol/l.) of either S or iodate and t is the time (hr). A nonintegral rate dependence, $[H^+]^{1+m}$ where m is close to 1 cannot be excluded on the basis of our data.

Discussion and Conclusions

Iodate reacts to form iodine at a significant rate even in a neutral buffered solution. The fact that the decomposition of iodate and S obey the same rate law is confirming evidence that S is, in fact, iodate.

We conclude that differences in the elapsed time between ozone collection and subsequent analyses may account for some of the discrepancy between previous investigations in which HC or IC ozone was absorbed. Differences in the quantity of iodate formed may also be an important factor.

Much less iodate was formed in these experiments than in that reported by Parry and Hern (*8*). This might be ascribed to differences in the ozone concentration (100–400 ppm vs. 1600–6000 ppm), a difference in the frits we used, a difference in the gas sampling rate, or to differences in solution pH. Since they only reported ozone concentration, we are unable to rule out any of these possibilities.

If iodate is also formed at IC with impingers, the decomposition (Equation 3) could explain the color development time reported by Saltzman and Gilbert (*11*) and Saltzman (*12*). The fading of color at long times in those reports then might be due to iodine volatilization or to side reactions.

However, Parry and Hern (*8*) reported negligible iodate at IC when they used an open glass tube as a bubbler; this seems to indicate that iodate would not be formed at IC with an impinger. We feel, nevertheless, that the four data points these investigators presented at unspecified values of other parameters do not provide sufficient information to draw a definite conclusion.

The acidification procedure, outlined here, provides a satisfactory method for the analysis of high ozone concentrations. This is in agreement with Schmitz (*15*). The procedure would not be suitable for lower levels of ozone (less than 50 ppm) because the iodide solution is slowly oxidized after acidification and this would lead to a significant error. However, this shortcoming might be overcome by using buffered acidification to a *controlled* pH level where the rate of iodate decomposition (Equation 3) is rapid, but where oxidation remains negligible. This acidification might also be performed in stages to minimize the total time during which the pH is low.

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Received for review September 11, 1974. Accepted February 18, 1975. Work supported by National Science Foundation Grant GK-37469.

Ambient Air Analysis with Dichotomous Sampler and X-ray Fluorescence Spectrometer

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■ Aerosol samples were collected in St. Louis using a dichotomous sampler operating on the principle of virtual impaction and were analyzed for a wide variety of elements by X-ray fluorescence. A striking difference was observed between the particles collected in the 0–2-μm range and the particles collected in the 2–10-μm range. Although nearly equal mass was collected in the two size ranges, the deposit of small particles was black and the deposit of the coarse particles was a light tan. At least 75% of the S, Zn, Br, and Pb occurred in particles smaller than 2 μm, and at least 75% of the Si, Ca, Ti, and Fe occurred in particles larger than 2 μm.

A major task in the field of air pollution monitoring is the development of devices for determining the mass and composition of airborne particulate matter as a function of size and time. This instrumentation is presently needed for human studies research in which attempts are being made to determine toxic threshold levels for aerosol constituents in ambient air. It is also needed for aerosol formation and transport studies essential to the development of cost-effective control strategies.

To perform elemental analysis on an increasing number of samples in more than one size range, a rapid analytical procedure is required. The use of X-ray fluorescence spectroscopy is well suited to meet this need for elements heavier than Al in atomic weight (*1, 2*). A wide variety of elements can be determined in a few minutes without sample preparation. The composition of the sample is determined by irradiating with a beam of X-rays and observing the emission of characteristic K and L X-rays. By use of secondary fluorescers to produce a nearly monochromatic but variable energy X-ray source, a wide variety of elements throughout the periodic table can be analyzed (*3*). If particles are collected on the surface of a membrane filter, then no sample preparation is required.

The sample collection device must be designed with consideration given to the nature of the aerosol and to the effects of the aerosol on human health. Recent measurements by Whitby et al. (*4*) show that the volume and hence the mass of aerosol in ambient air has a bimodal distribution with a relative minimum at particle diameters of about 2 μm. It has been established that particles smaller than 3.5 μm in diameter can penetrate deeply into the human respiratory system, and that larger particles are trapped in the upper respiratory passages (*5*). For these reasons, it is desirable to use a dichotomous sampler to collect particles in two size ranges rather than to collect total particulates on a single filter. Separation at particle diameters of about 2 μm would be appropriate for aerosol research; separation at 3.5 μm is needed for monitoring aerosols to protect human health. Fractionation of particles into several additional size ranges is desirable only if the increased cost of analyzing more stages and the decreased deposited mass per stage can be tolerated.

For size fractionation, a wide variety of conventional impactor devices is available in which particles are collected on a surface placed behind a circular or slit-shaped orifice.

Collection in these devices may not be quantitative if particles bounce off the intended collection surfaces. Particle bounce errors can be reduced by applying an adhesive coating to the collection surface (*6*). However, Lundgren has demonstrated that the effectiveness of the adhesive coating can become nullified when a monolayer of particles has been deposited (*7*).

The problems inherent in collection by impaction onto surfaces can be eliminated by using a virtual impactor in which particles are impacted into a slowly pumped void (*8, 9*). Figure 1 illustrates a dichotomous sampler (a device which collects particles in two size ranges) which operates on the principle of virtual impaction. In this device, the air being sampled passes through an inlet jet and is deflected around a coarse particle receptor. Coarse particles, unable to follow the curving air stream, enter the coarse particle receptor and are collected on a filter. Fine particles that move with the air stream are collected on a second filter. The use of filters in a virtual impactor eliminates the particle bounce problem associated with impaction surfaces.

To minimize wall losses in the virtual impactor, it is necessary to maintain a small flow of air into the coarse particle receptor. In the device illustrated in Figure 1, critical flow orifices are used to maintain a 7:1 concentration ratio between inlet and coarse particle air streams. For this flow ratio, 14.3% of the fine particle mass is deposited on the coarse particle filter.

To reduce the contamination of fine particles on the coarse particle filter, two virtual impactors, which have the same fractionation cutpoint diameters, can be operated in series. Figure 2 illustrates a practical two-stage device developed by Peterson (*10*). An internal orifice maintains a 7:1 concentration ratio for each stage, and external orifices maintain an overall concentration ratio of 49:1 for the inlet and coarse particle air streams. For this flow ratio, only 2% of the fine particle mass is collected on the coarse particle filter. Attempts have been made to develop a single-stage virtual impactor with a 49:1 concentration ratio, but wall losses were much worse than those obtained using a two-stage device (*10, 11*).

In the present work, a prototype dichotomous sampler was field tested and evaluated for usefulness as an ambient air monitor. Aerosols collected in the dichotomous sampler and in a second automatic filter changing device were analyzed for elemental content with an X-ray fluorescence spectrometer.

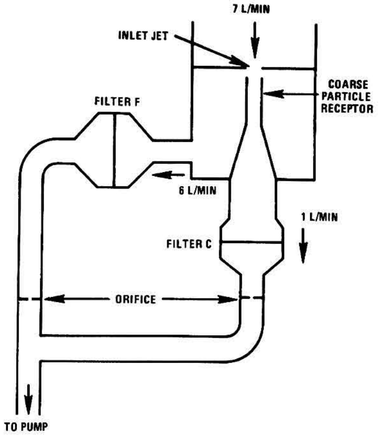

Figure 1. Schematic view of dichotomous sampler that contains a single-stage virtual impactor

Flow rate at inlet is 7 l./min, and the concentration ratio for coarse particles is 7:1. Coarse particles are collected on filter C; fine particles are collected on filter F

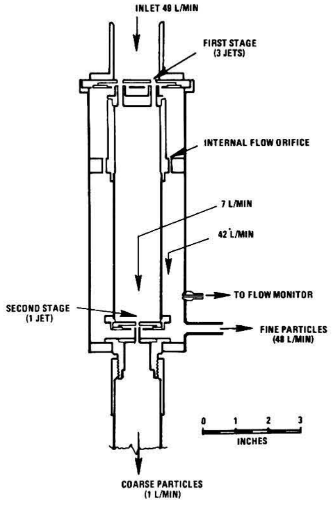

Figure 2. Drawing of dichotomous sampler with two substages used in present work

Each substage has the same fractionation cutpoint diameter. The internal flow orifice and orifices in exit flow lines (not shown) together maintain a 7:1 concentration ratio for each stage

Experimental

The dichotomous sampler used in this study is illustrated in Figure 2 and was built by Environmental Research Corp. (St. Paul, Minn.). It was evaluated for wall losses and fractionation characteristics by Loo and Jaklevic (*12*) using monodisperse aerosols of dioctylphthalate. It was demonstrated that particles smaller than 2.0 μm (50% cutpoint diameter) were collected on the fine-particle stage, and particles ranging from 2.5–10 μm (50% cutpoint diameters) were collected on the coarse particle stage. Wall losses were very low for particles smaller than 1 μm and for particles between 3.5 and 8 μm. The wall losses were about 25% in the 2–3-μm range of diameters and were large for particles larger than 10 μm (*12*).

The dichotomous sampler was operated with the flow rate divisions indicated in Figure 2. Flow rates were checked at the beginning and end of each measurement using a dry test meter. The inlet flow rate was maintained at 49 l./min within an accuracy of ±3%. A second sampling device which automatically changed the filter every 2 hr was also used. This device also operated at a flow rate of 49 l./min, and used a single collection surface without size fractionation.

Measurements of trace element composition were made using an energy dispersive X-ray fluorescence spectrometer (*3*) which is illustrated in Figure 3. In this device, an X-ray beam from the tungsten anode excites the secondary fluorescer which in turn excites the sample with its nearly monochromatic characteristic X-rays (*13*). The three fluorescers used are Cu, Mo, and Tb, for which the corresponding anode potentials of the X-ray tube are 35, 50, and 70 kV, respectively. Each sample was analyzed for 5 min with each fluorescer with an electron current of 400 μA in the X-ray tube. The fluorescent X-ray lines emitted by the sample were detected in a lithium-drifted silicon detector which used electronic collimation to enhance the signal

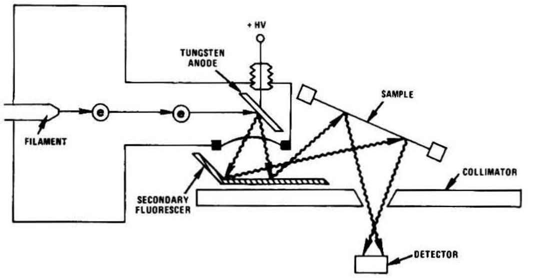

Figure 3. Schematic view of X-ray fluorescence spectrometer using secondary fluorescer and solid state detector

above background (*3*). Because of the very compact geometrical arrangement of the components in Figure 3, an adequate count rate was obtained with X-ray power dissipation of less than 30 W.

The ability of the system to detect a wide variety of elements in the atmosphere is illustrated in Figure 4, which is a plot of the ranges and typical values of the concentrations of various elements in urban air (*15*). The detection limits (3σ peak area above background) for X-ray fluorescence are superimposed on the plot. These detection limits are expressed in ng/cm^2 for each element assuming that it is deposited on a cellulose membrane filter which has a mass per unit area of 5 mg/cm^2. The discontinuities in the detection limit curve using the molybdenum fluorescer are due to iron and copper impurities in the X-ray collimator above the detector. The detection limits can be converted to units of mass per unit volume by dividing the values on Figure 4 by the air volume sampled per unit area of filter. For a flow rate of 49 l./min through an 8-cm^2 area of filter, the conversion factors are 0.74 m^3/cm^2 for a 2-hr sampling interval and 8.8 m^3/cm^2 for a 24-hr sampling interval.

For X-ray analysis it is necessary that particles be collected on a filter having very low levels of impurities. Figure 5 shows a spectrum of a Teflon membrane filter with a polyethylene backing which is excellent in this regard. Figure 5 also shows a spectrum of clean glass fiber filter which contains large amounts of impurities and is unacceptable for X-ray fluorescence analysis. Membrane filters, made of mixed esters of cellulose and having 0.8-μm pore size, make a good choice and were used in this work. Their elemental purity is similar to that of the Teflon shown in Figure 5 except for impurities of Ca and Cl. High-porosity Teflon with superior gravimetric characteristics became available after the experimental phase of this work was completed.

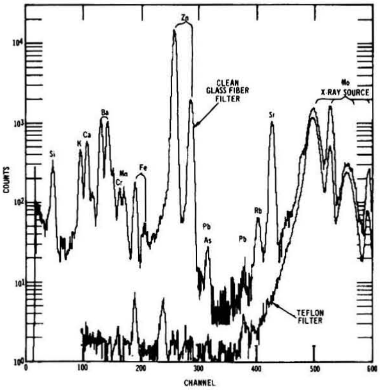

Figure 5. X-ray spectra of clean polyethylene-backed Teflon filter and clean glass fiber filter using molybdenum secondary fluorescer for excitation

In Teflon filter spectrum, peaks in channels 188 and 238 are due to iron and copper impurities in collimators of X-ray spectrometer

The elemental concentrations were determined by a minicomputer interfaced to the X-ray spectrometer. For the analysis, it was assumed that an observed X-ray spectrum was a superposition of characteristic X-rays of each individual element in the sample. Individual spectra of 40 pure element standards were accumulated and stored in the computer memory. These individual spectra as well as

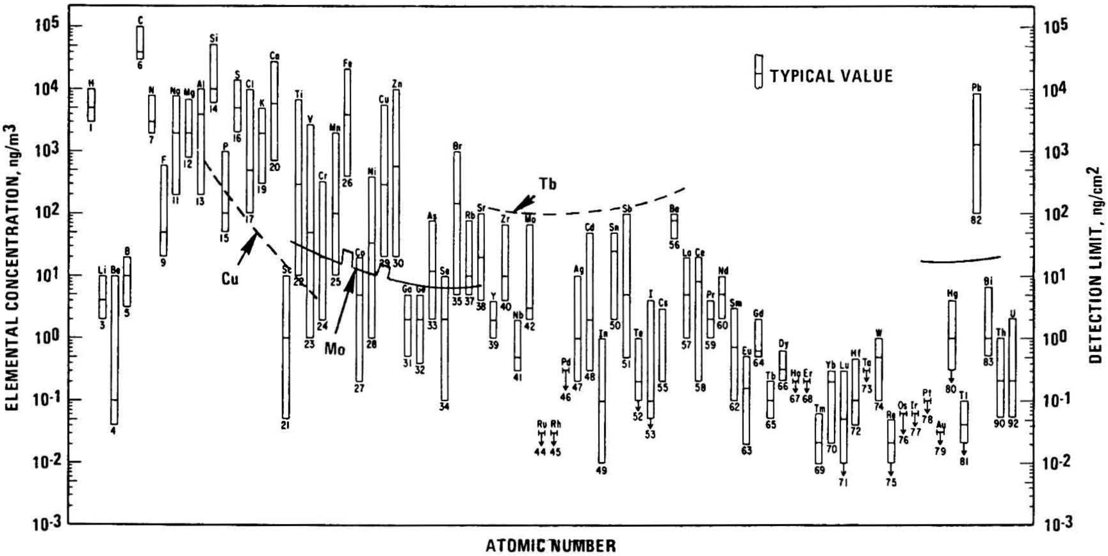

Figure 4. Detection limit curves using Cu, Mo, and Tb fluorescers expressed in ng/cm^2

Conditions of analysis and substrate are specified in the text. Also shown are ranges and typical values of urban trace element concentrations compiled by Cooper (*14*) a stored clean filter background spectrum were compared with the unknown aerosol spectrum using a stripping procedure to determine the concentration of each element (*3*). By making a judicious choice of the order in which the elements were stripped, the problem of interfering K_α and K_β X-ray lines was largely eliminated.

The analyzer was calibrated using thin single-element concentration standards according to a procedure developed by Giauque et al. (*1*). These standards consisted of vacuum evaporated foils obtained from Micromatter Co. (Seattle, Wash.) and dried solution deposits on membrane filters obtained from Columbia Scientific Industries (Austin, Tex.). The elemental deposits were uniform across the 37-mm diameter of each standard and ranged in mass per unit area from 10–150 $\mu g/cm^2$. They were known to an accuracy of ±10% or better.

For airborne particulates uniformly deposited onto a 37-mm diameter filter, the concentration (in $\mu g/cm^2$) of a specific element on the filter was determined by comparison of the observed count rate with that of the known foil of the same element. A smooth curve was fitted to the calibration points and used to determine elements for which foils were not available or not accurately known. By use of the smooth calibration curve, the root mean square deviation of the X-ray analysis of each calibration foil from the gravimetric value was 5% for the elements with atomic numbers between 19 and 38.

From these considerations it is estimated that for elements well above the detection limit, the 1-σ accuracy for X-ray analysis of elements with atomic numbers above 20 (Ti and heavier) is ±10%. This is compatible with the results from a recent study by Hammerle et al. (*15*) in which X-ray fluorescence and neutron activation analyses were applied to aerosol samples, and 20% agreement was obtained. For the lighter elements the energies of the characteristic X-rays are sufficiently low that significant self-absorption can take place within the larger collected particles and within the filter media for fine particles that penetrate into the filter. Self-absorption corrections were made, using a procedure developed by Dzubay and Nelson (*16*).

For the two size ranges of the dichotomous sampler, the total aerosol mass was determined by gravimetrically comparing the weights of each filter before and after sampling. A ^{210}Po radioactive source was placed inside the microbalance chamber near the weighing pan to eliminate electrostatic effects. Gravimetric accuracy was ±50 μg for the filters, which had typical deposit masses of about 1–2 mg.

Results and Discussion

Samples were collected over the period between August 26 and August 31, 1973, in St. Louis at a site on the Washington University campus. Figure 6 shows a photograph of two filters used in the dichotomous sampler for the 23-hr period beginning at 0915 hr on August 30. X-ray spectra for these filters are shown in Figure 7, and the elemental and gravimetric analyses are shown in Table I. The results for five days of continuous measurements using 2-hr sampling periods with unfractionated aerosol are shown in Figures 8 and 9.

The filters shown in Figure 6 indicate the striking difference between small and large particles. The large particles produce a light tan deposit, and yet they have almost as much total mass as the small ones, which make a black deposit. This is consistent with the notion that the large particles contain large amounts of earthen crustal materials, whereas the small particles consist of combustion and secondary aerosols. From the analysis of the two filters in Table I, it appears that the large particles contain at least

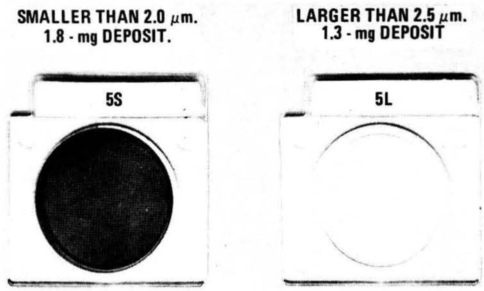

Figure 6. Photograph of filters used in dichotomous sampler for 23-hr period beginning at 1015 hr, August 30, 1973, in a St. Louis residential neighborhood

Volume sampled is 68 m^3. Filters are mounted in 5.1 × 5.1-cm frames used for automatic manipulation within X-ray analyzer. Elemental analysis for these samples is given in Table I

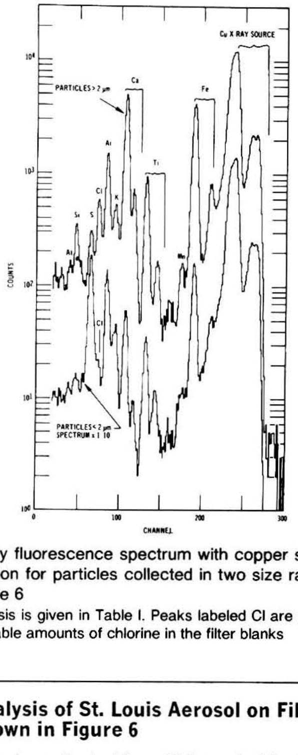

Figure 7. X-ray fluorescence spectrum with copper secondary fluorescer excitation for particles collected in two size ranges on filters shown in Figure 6

Elemental analysis is given in Table I. Peaks labeled Cl are partly due to significant but variable amounts of chlorine in the filter blanks

Table I. Analysis of St. Louis Aerosol on Filters Shown in Figure 6

Samples collected for a 23-hr period beginning 1015 hr August 30, 1973

Element	Fine,[a] ng/m^3	Coarse,[a] ng/m^3	Element	Fine,[a] ng/m^3	Coarse,[a] ng/m^3
Si	600 ± 160	2000 ± 700	Zn	45 ± 6	15 ± 2
S	3700 ± 600	600 ± 200	As	20 ± 10	<4
K	160 ± 60	240 ± 80	Se	7 ± 2	<2
Ca	110 ± 40	1700 ± 300	Br	114 ± 12	30 ± 4
Ti	64 ± 7	210 ± 30	Rb	<1	<1
V	4 ± 2	<3	Sr	<2	4 ± 2
Cr	<3	<3	Cd	<13	<13
Mn	5 ± 2	6 ± 2	Sn	<14	<14
Fe	130 ± 14	400 ± 40	Ba	<30	<30
Co	<2	<2	Pb	460 ± 50	110 ± 12
Ni	<2	<2	Gravimetric	26,600 ± 800	19,200 ± 800
Cu	<3	<3			

[a] The collected size ranges are 0–2 µm for fine particles and 2.5–10 µm for coarse particles.

Table II. Maximum Amount of Various Sulfate Compounds Deduced from Observed Elemental Sulfur and Metal Concentrations Listed in Table I for Particles Smaller Than 2 μm

It is assumed that all of the sulfur is in the form of sulfate

Compound	Sulfate, %[a]	Compound	Sulfate, %[a]
K_2SO_4	<2%	$Fe_2(SO_4)_3$	<3%
$CaSO_4$	<3%	$ZnSO_4$	<1%
$Ti_2(SO_4)_3$	<2%	$PbSO_4$	<2%

[a] If only fraction F of the elemental sulfur were in the form of sulfate, then these percentages are to be multiplied by 1/F.

75% of the Si, Ca, Ti, and Fe at the sampling site. At least 75% of the S, Zn, Br, and Pb is contained in the small particles. These same features were observed in all the data from the dichotomous sampler over the August 26–31 sampling period. Similar results have been reported by Lee et al. (*17*) for a variety of elements. The concentrations listed in Table I for V, Cr, Mn, Ni, Cu, Zn, Rb, and Sr are significantly lower than the typical urban values shown in Figure 4. This may be due to the residential nature of the sampling site and to the relatively clean air conditions at the time of measurement. Variable amounts of chlorine in the filter blanks prevented analysis for that element.

In these data the most abundant observed element is sulfur. Certain sulfate compounds such as zinc ammonium sulfate, sulfuric acid, and ammonium sulfate have been shown by Amdur (*18*) to be pulmonary irritants. If one makes the assumption that all sulfur is in the form of sulfate, then one can deduce the maximum possible fraction of the sulfate that is associated with the various observed cations as shown in Table II. One notes that the biologically active zinc sulfate compounds can only be minor components. Table II suggests that significant amounts of sulfate may be bound to light element cations such as H^+ or $(NH_4)^+$. Additional work needs to be done to demonstrate the accuracy of the X-ray analysis for sulfur, to determine the percentage of sulfur in the form of sulfate and to verify that the observed sulfur is not the result of SO_2 being converted to sulfate on the filter.

The diurnal patterns of the elements plotted in Figures 8 and 9 give valuable clues about the source of these pollutants. For example, the enormous fluctuation in the titanium concentration is indicative of a local discrete source. The lack of major fluctuations in the sulfur concentration indicates a lack of a single local or discrete source. The Br to Pb ratio and the lead concentration seem to be influenced by rush hour traffic patterns.

These results illustrate the utility of using the combination of dichotomous sampler, X-ray fluorescence analyzer and gravimetric analysis for particulate monitoring. For future studies of this type, a newly developed dichotomous sampler will be available. Through careful design by Loo (*11*), the wall losses in the 0–15-μm range of diameters are reduced to a very low level. Ten dichotomous samplers with automatic sample changers are presently being installed in a network for use in the Regional Air Pollution Study in St. Louis. A second low loss dichotomous sampler has been developed for routine field use (*19*).

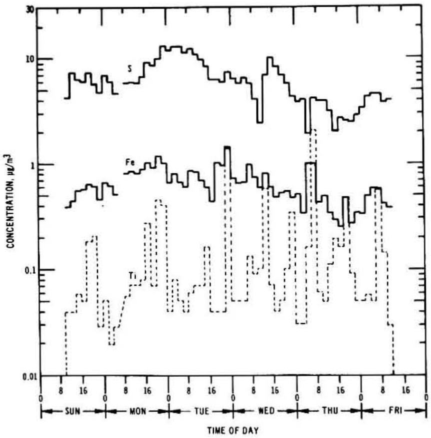

Figure 8. Plot of 2-hr average concentrations of S, Fe, and Ti for the five-day period between August 26 and August 31, 1973, in St. Louis
Size fractionation was not used

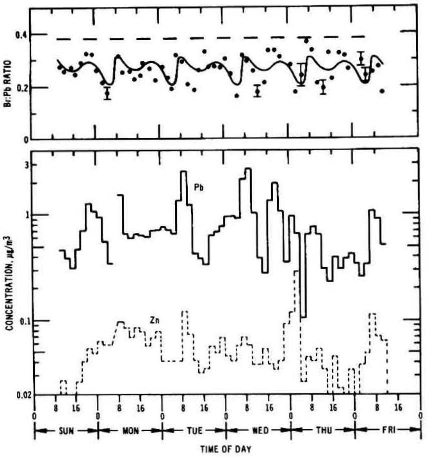

Figure 9. Plot of 2-hr average concentrations of Zn, Pb, and the Br–Pb ratio for period between August 26 and August 31, 1973, in St. Louis
Smooth curve is a repetitive 24-hr pattern and guide to the eye. Size fractionation was not used

Acknowledgments

The authors are grateful to F. S. Goulding, J. M. Jaklevic, B. V. Jarrett, J. Meng, and H. A. Rook for valuable advice and discussions, to J. A. Cooper for providing the plot of elemental abundances used in Figure 4, to W. E. Wilson for providing space in his mobile laboratory in St. Louis to operate the sampling equipment, and to W. C. Peters and C. R. Sawicki and L. E. Hines for valuable assistance.

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Received for review July 11, 1974. Accepted April 10, 1975. Mention of commercial products is for identification only and does not constitute endorsement by the Environmental Protection Agency of the U.S. Government.

Distribution of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) in Aquatic Model Ecosystem

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■ Several organisms in a model ecosystem were exposed to ^{14}C-labeled TCDD for up to 31 days to determine the distribution and bioaccumulation potential in the aquatic environment. TCDD accumulation by all organisms was directly related to water concentration (0.05–1330 ppt) and averaged 2.0–2.6 × 10^4 (snail, *Gambusia*, and daphnid) and 4–9 × 10^3 (duckweed, algae, and catfish) times the water concentration. No metabolites of TCDD were found in submerged soil, water, snails, *Gambusia*, or catfish.

Discovery in 1970 of the highly toxic contaminant 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in the herbicide (2,4,5-trichlorophenoxy) acetic acid (2,4,5-T) spawned a great deal of concern about the potential hazard to man and the environment. This concern subsequently stimulated numerous studies to assess the behavior of TCDD in the environment [as summarized by Helling et al. (*1*)]. These studies revealed that TCDD is immobile in soils, is not translocated in plants, has a half-life in soil of about 1 year, and is slowly photodecomposed in water but not on soil. The results of these studies, combined with the knowledge that presently produced 2,4,5-T contains <0.1 ppm TCDD, indicate that TCDD is not entering or being distributed in the environment in large quantities. However, concern still lingers over the TCDD hazard to man for several reasons: (1) it has an extremely high mammalian toxicity [LD_{50} of 10 μg/kg for rabbits (*2*)]; 0.6 μg/kg for guinea pigs (*3*); (2) it is a teratogen (*4, 5*); and (3) concentrations of TCDD ranging from about 20–1000 parts per trillion (ppt) have been found in fish and crustaceans from South Vietnamese waters (*6*). Since this concern exists and the total environmental impact is still in question, we felt that further information on the probable environmental distribution would be useful. This study was therefore initiated to determine the availability, distribution, and bioaccumulation potential of TCDD in a model ecosystem.

This model ecosystem was designed to simulate the usual mode of entry of pesticides into water and the simultaneous exposure of several organisms representing parts of natural food chains. The bulk of pesticides (or their contaminants) that enter water unintentionally do so via erosion of pesticide contaminated soil or plant remains from agricultural land. The amount of pesticide that enters water from the submerged soil will depend on its solubility and desorption from soil. Simultaneous exposure of several organisms should ensure that accumulation by all processes—i.e., absorption, adsorption, and consumption of lower by higher food chain organisms, would be represented. As designed, this model ecosystem exposes both a test chemical and organisms to some of the major conditions that might realistically be expected to occur in the environment. The system is not designed to determine the effects of a chemical on the organisms (though some primary effects can be assessed) but rather, how does the chemical behave when subjected to likely environmental conditions.

Experimental

One single concentration and two multiple concentration experiments were performed. In each, ^{14}C-TCDD was adsorbed to soil, and placed in the bottom of glass aquaria (25.4 × 5.2 × 17.8 cm). Table I summarizes the treatment, rate, and replication details of the three experiments. In

Table I. Soil TCDD Application Rates and Replications

Total TCDD added per tank, μg	Type and amount, grams, of soil combined with TCDD[a]	Final soil TCDD concn., ppm[b]	No. of replicates
	Experiment I		
149	L-20	7.45	3
0	L-20	0	1
	Experiment II		
63	L-20	3.17	2
63	L-20 + M-100	0.53	2
63	L-20 + M-200	0.29	2
63	L-20 + M-400	0.15	2
0	L-20	0	2
	Experiment III		
10	M-100	0.1	2
1	M-100	0.01	2
0.1	M-100	0.001	2
0.01	M-100	0.0001	2
0	M-100	0	2

[a] L = Lakeland sandy loam, M = Matapeake silt loam. In II, L was first treated with TCDD, then dry mixed with M in treatment tanks.
[b] Soil concentrations based on total quantity of soil in tank.

experiment II, TCDD was first added to Lakeland sandy loam soil (pH 6.2; organic matter content 0.9%; and sand, silt, and clay contents of 71.6, 16.4, and 12.0%, respectively) and then dry mixed with Matapeake silt loam soil (pH 5.3; organic matter content 1.5%; and sand, silt, and clay contents of 38.4, 49.4, and 12.2%, respectively) in the tanks before water was added. Twenty grams of untreated Lakeland and 100 grams of untreated Matapeake soil were placed in the bottom of the control tanks in experiments I and II and III, respectively. Ring-labeled TCDD (specific activity 2.8 μCi/mg and 460 μCi/mg) was used in experiments I and II, and III, respectively.

Preparation, operation, and sampling of the ecosystems have been described (7). In brief, control of TCDD-treated soils were placed in tanks, which were then filled with 4 liters of water. One day later ~100 daphnids (*Daphnia magna*), eight snails (*Physa* sp.), a few strands of an alga (*Oedogonium cardiacum*), and 10 ml of old aquarium water containing various diatoms, protozoa, and rotifers were added. In experiment III, ~15 duckweed (*Lemna minor*) plants were added. Water samples, taken at 2-day intervals, were assayed for radioactivity using standard liquid scintillation methods. At 30 days, samples of daphnids were taken for analysis, and two mosquito fish (*Gambusia affinis*) were added to each tank. Three days later all organisms were harvested. In experiments II and III, two fingerling channel catfish (*Ictalurus punctatus*) were added to each tank after all other organisms were harvested and exposed for 6 days.

The aquatic organisms represent parts of two food chains: water → algae → snails and water → diatoms, protozoa, and rotifers → daphnids → fish. These chains overlap somewhat since snail excreta probably provided some food for diatoms, protozoa, rotifers, and daphnids.

The concentration of TCDD in water at the end of the experiment was determined as follows. In experiment I, 1-ml samples of filtered water were directly analyzed by standard liquid scintillation counting. In experiments II and III, water centrifuged at 5860 × g for 1 hr was concentrated. In experiment II, 20 ml was taken to dryness and counted, whereas in experiment III, 500 ml was reduced to 10 ml. The 10-ml concentrate was analyzed by counting two 1-ml samples and reducing 5 ml to dryness, combusting the residue and collecting and analyzing the $^{14}CO_2$ as described below.

Snails, *Gambusia*, and catfish were homogenized whole in methanol and filtered. Radioactivity in the filtrate was assayed by scintillation counting. Residues (after extraction) of snails, *Gambusia*, and catfish, and samples of algae, duckweed, and daphnids were dried at 60°C to obtain dry weight and then combusted in a stream of oxygen. The $^{14}CO_2$ was dried by passing through a column of anhydrous $CaSO_4$ and trapped in 10 ml of monoethanolamine/2-methoxyethanol (1:7 by volume). A 5-ml aliquot of the trapping solution was assayed for radioactivit by standard liquid scintillation methods. TCDD was calculated as a total of ^{14}C in combusted samples (algae, duckweed, and daphnids) and as a sum of ^{14}C in the combusted extracted residues plus methanol filtrate. The filtrate (from snails, *Gambusia*, and catfish) usually contained >80% of the total ^{14}C.

Thin-layer chromatography (TLC) analysis was determined on certain components to assess the extent of TCDD degradation, if any. Extracts (experiment III only) of snails, *Gambusia*, and catfish (from 0.1- and 0.01-ppm treatment rates) and hexane extracts of water (from 0.1-ppm rate) were spotted on silica gel TLC plates. Moist 1-gram soil samples (experiment III, 0.1-ppm rate) were extracted with 30-ml acetone:hexane (1:1) and the extract was spotted as above. The TLC plates were developed with cyclohexane:chloroform (80:20) and radioautographed.

Soil samples from all treatments were dried, combusted, and analyzed as described above to determine total residual TCDD at the end of the experiments.

Results and Discussion

The amount of TCDD in water reached equilibrium in 4 (experiment I, and the 3.17-ppm rate of experiment II) and 15 (0.1- and 0.01-ppm rates of experiment III) days after the start of the experiments. Radioactivity was too low for measurement in 1 ml of water at the other rates. The difference in equilibrium times probably reflects the adsorb-

Table II. Bioaccumulation of ^{14}C-TCDD by Several Aquatic Organisms as Affected by Soil and Water Concentration

Expt[a] no.	Soil concn, ppm	H_2O concn, ppt	Ppb					
			Algae	Duckweed	Snails	Daphnids	Gambusia	Catfish
I	7.45	1330	6690 ± 960[b]	Na[c]	1820 ± 170	10,400 ± 480	1380 ± 220	na
II	3.17	239	2500 ± 120	Na	2780 ± 400	7,450 ± 30	2200 ± 680	720 ± 130
II	0.53	48	390 ± 20	Na	1970 ± 690	<70	540 ± 250	110 ± 90
II	0.29	18	230 ± 20	Na	290 ± 30	<70	420 ± 190	120 ± 5
II	0.15	7	130 ± 50	Na	330 ± 80	<70	90 ± 20	80 ± 50
III	0.10	7.13	79.3 ± 12.5	30.7 ± 1.3	125 ± 23	163 ± 10	439 ± 76	103 ± 49
III	0.01	0.66	5.0 ± 1.0	3.3 ± 0.5	9.7 ± 1.4	17.7 ± 5.9	41.8 ± 4.5	18.4 ± 5.3
III	0.001	0.26	1.4 ± 0.2	0.3 ± 0.0	1.4 ± 0.2	4.7 ± 2.2	5.9 ± 2.7	1.2 ± 0.3
III	0.0001	0.05	0.1 ± 0.0	0.2 ± 0.1	1.2 ± 0.6	2.4 ± 1.1	1.2 ± 0.6	0.1 ± 0.0
			Bioaccumulation Ratio[d]					
I		1330	5,000	na	1,400	7,800	1,000	na
II		239	10,500	na	11,600	31,200	9,200	3,000
II		48	8,100	na	41,000	na	11,300	2,300
II		18	12,800	na	16,100	na	23,300	6,700
II		7	18,600	na	47,100	na	12,900	11,400
III		7.13	11,100	4300	17,500	22,900	61,600	14,400
III		0.66	7,600	5000	14,700	26,800	63,300	27,900
III		0.26	5,400	1200	5,400	18,100	22,700	4,600
III		0.05	2,000	4000	24,000	48,000	24,000	2,000

[a] TCDD of 2.8 μCi/mg specific activity used in experiments I and II; 460 μCi/mg specific activity used in experiment III. [b] Standard error of the mean for 3 replications (experiment I) and 2 replications (experiments II and III). [c] Na-Not analyzed. [d] Concentration of TCDD in tissue (dry wt) divided by concentration of TCDD in water.

ing medium—i.e., 20 grams of Lakeland soil (low adsorptive capacity) for experiments I and II and 100 grams of Matapeake soil (higher adsorptive capacity) for experiment III. At equilibrium, TCDD removed from water by accumulation by organisms, adsorption to glass and detritus, and volatilization was probably replaced through desorption from soil. With the exception of the two lower rates in experiment III, soil served as a reservoir which contained more TCDD than could theoretically dissolve [0.8 μg/4 l., assuming a water solubility of 0.2 ppb (*8*)]. Water concentration was at or below the maximum water solubility of TCDD for all rates except experiment I. Water from experiment I was filtered only before analysis and may have contained suspended particulate matter not present in the centrifuged water from experiments II and III. Sediment recovered after centrifugation did contain radioactivity.

Experiment I was a preliminary, single rate study designed to determine what bioacculumation magnitude might be expected and how aquatic organisms would respond to this toxic material. Experiments II and III were multiple rate studies designed to determine the effect of soil adsorption on TCDD availability to aquatic organisms. All organisms in both treatment and control tanks prospered (daphnids increased in population and snails laid numerous egg clusters on tank walls) during this exposure period, indicating that TCDD was not toxic at the concentrations used. In experiment I (highest exposure rate), organisms accumulated 1.4–10.4 ppm (Table II), which exceeds the acute oral, single-dose toxicity (LD_{50} = 10 μg/kg) to rabbits (*2*) by 10^2 to 10^3 times. *Gambusia* and catfish were exposed for 3 and 6 days, respectively, which may have been an inadequate period for toxicity to develop.

The bioaccumulation ratios obtained in this study were higher than the concentration factors obtained by Matsumura and Benezet (*8*). However, the experimental conditions used in the two studies were considerably different—i.e., we used a longer exposure time, different organisms, a larger system design, and a wider range of water concentrations. One of their models that was somewhat similar to our system did yield a concentration factor of 9200 for mosquito larvae, which compared well with the accumulation ratios we obtained. Matsumura and Benezet (*8*) calculated their concentration factors on a fresh weight basis while we calculated our bioaccumulation ratios on a dry weight basis. Conversion of our ratios to a fresh weight basis significantly lowers the ratios, but most are still well above their factors.

The TCDD concentration in the organisms approximately equaled (usually within one order of magnitude) the concentration of TCDD in the soil, whereas water contained an average of 0.015% as much as soil (Table II). Some bioconcentration between elements of the food chain (algae and duckweed to snails, and to a lesser extent, daphnids to *Gambusia*) was observed, but inconsistent results at some concentrations make the importance of this observation unclear. Accumulation of different quantities of TCDD by various organisms could simply indicate a species specificity. However, for most other pesticides that have been tested in the ecosystem, the lower food chain organisms, algae and daphnids, usually contain greater concentrations than higher food chain organisms, snails and *Gambusia*.

Fingerling catfish always contained less TCDD than *Gambusia*, even though catfish were exposed 3 days longer. Catfish are bottom feeders and presumably could consume large amounts of TCDD incorporated in the detritus. Fish accumulate residues directly from water as well as by ingesting contaminated food. Some workers have found that adsorption accounts for most of the chlorinated hydrocarbon pesticide residues found in several aquatic organisms (*9*). Since catfish used in this experiment were much larger than *Gambusia* (average dry weight was 6.7 times higher) and therefore have smaller surface area to mass ratios than *Gambusia*, adsorption may partly account for the different residue levels.

In experiment II, for three of the four concentrations, TCDD content in daphnids was below the level of detection (70 ppb) probably caused by small sample size and low specific activity of TCDD.

The bioaccumulation ratios fluctuated considerably over the range in concentration for each organism, and the averages ranged from 2–2.6 × 10^4 for snails, *Gambusia*, and daphnids and 4–9 × 10^3 for duckweed, algae, and catfish. In comparison, *Daphnia magna* accumulated 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT), 1,2,3,4,10,-10 - hexachloro - 1,4,4*a*,5,8,8*a* - hexahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene (aldrin), and hydroxydimethylarsine oxide (cacodylic acid) at 11.4 × 10^4, 14.1 × 10^4, and 0.16 × 10^4 times the water concentration, respectively (*7*, *10*). Therefore, daphnids accumulated an average of 16 times more TCDD than cacodylic acid and about ⅕ as much as DDT and aldrin. These ratios indicate that TCDD has a considerable potential to bioaccumulate in the environment.

Highly significant correlation coefficients of 0.94 or higher were obtained between TCDD concentration in the organism and water (Figures 1–3). This high correlation over such a wide range in water concentration suggests that the amount of TCDD accumulated by aquatic organisms is controlled almost entirely by the amount of TCDD available in water.

A good correlation between TCDD content in soil and tissue or water could probably have been made. However, since none of the organisms used in this study are inhabitants of bottom mud or soil, direct uptake from soil was presumed to be minor compared to accumulation from water and consumption of other organisms.

Methanol extracts of *Gambusia*, snail, and catfish and hexane extracts of tank water and soil were analyzed by TLC (Figure 4). Of the recovered activity 86–94% was found in a single mobile spot for each sample. The lower mobility of tissue and water extract spots, as compared to

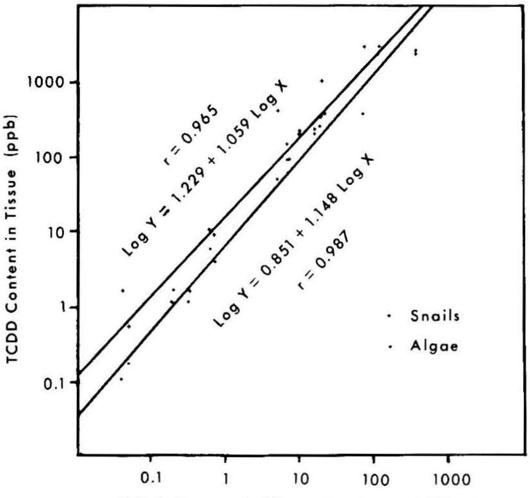

Figure 1. Correlation between concentrations of TCDD in snails and algae and in water over nine application rates in model ecosystem

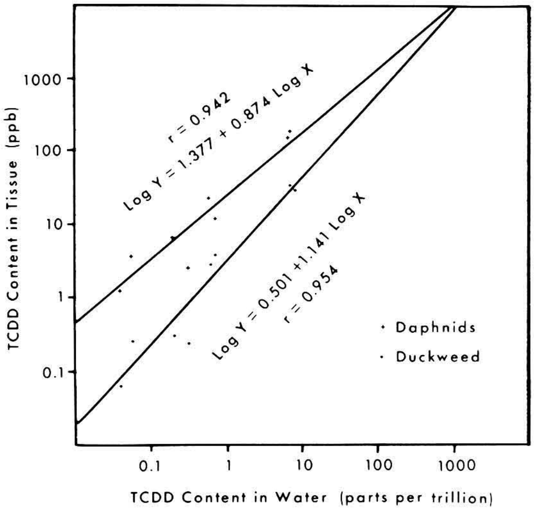

Figure 2. Correlation between concentrations of TCDD in daphnids and duckweed and in water over nine application rates in model ecosystem

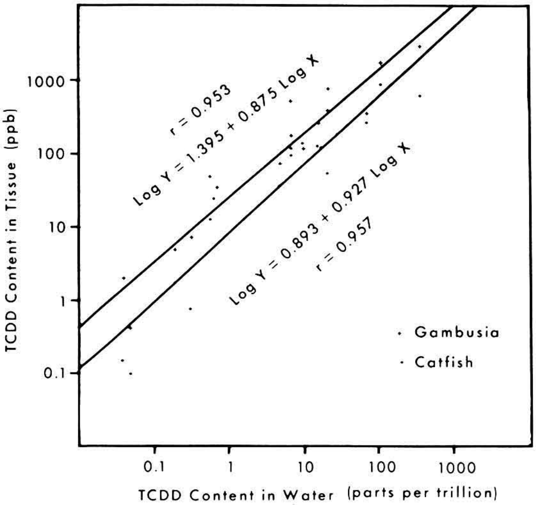

Figure 3. Correlation between concentrations of TCDD in *Gambusia* and catfish and in water over nine application rates in model ecosystem

the standard (R_f 0.71), may have been due to soluble organic material present in the extracts (as indicated by a yellow color). One and 3 ml of tissue extract were spotted from 0.1- and 0.01-ppm treatments, respectively. All of the hexane extract from 100 ml of centrifuged water was spotted. Some activity remained at the origin (1.9–5.9%) and as a streak (3.8–10.1%) between the origin and mobile spot. Radioactivity that remained below the mobile spot may also have been TCDD that was retarded through adsorption to the silica gel or glass. A mobile standard spot was scraped, extracted with benzene, spotted and run on another TLC plate. Distribution of radioactivity was identical to the original, indicating that TCDD adsorption to the plate may be responsible for the origin and streak components. Similar chromatographic behavior between sample extracts and the standard indicate that TCDD had not been degraded in any of these components of the ecosystem. However, since no extraction was 100% efficient, the nature of the remaining activity is unknown.

The amount of ^{14}C detected in water and tissue at the

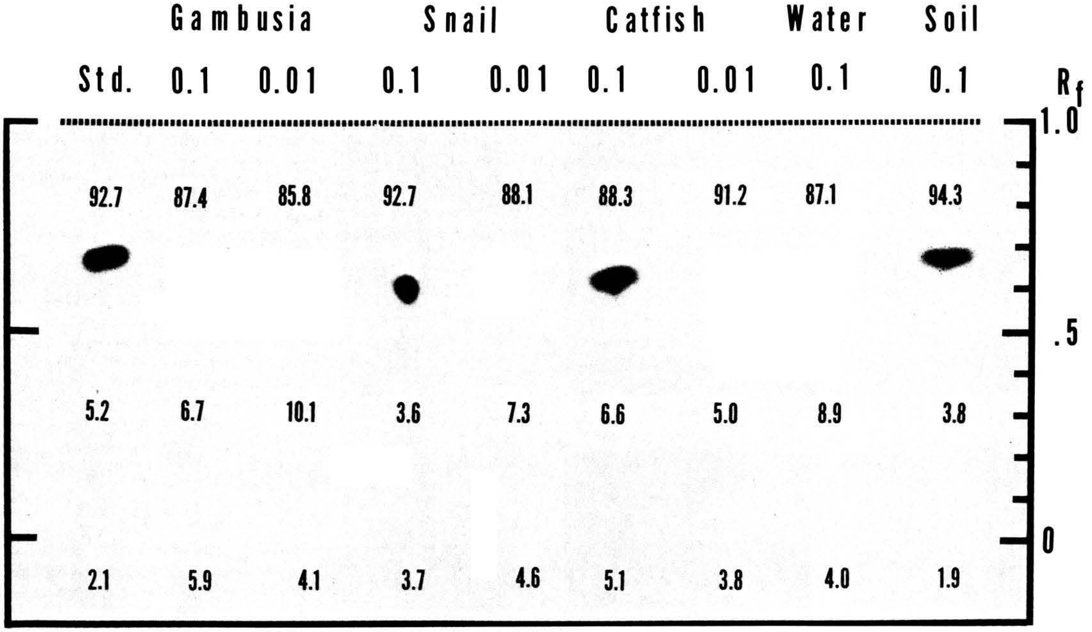

Figure 4. Radioautograph of *Gambusia*, snail, catfish, water, and soil extracts from 0.1- and 0.01-ppm treatment rates of experiment III
Numbers in graph refer to percent of total ^{14}C spotted that was recovered at origin (bottom numbers), streaked between origin and mobile spot (center numbers), and in mobile spot (top numbers)

Table III. Recovery of ^{14}C in Ecosystem Components

Expt. no.	Soil concn. ppm	Percent of ^{14}C-TCDD originally added								
		Soil	H_2O	Algae	Duckweed	Snails	Daphnids	*Gambusia*	Catfish	Total
I	7.45	84.90	3.61	1.90	Na[a]	0.44	0.16	0.06	Na	91.07
II	3.17	97.79	1.51	0.67	Na	0.23	0.02	0.04	0.20	100.46
II	0.53	95.09	0.30	0.12	Na	0.04	Nd[b]	0.02	0.04	95.61
II	0.29	88.45	0.11	0.06	Na	0.02	Nd	0.01	0.04	88.69
II	0.15	87.57	0.05	0.04	Na	0.02	Nd	<0.01	0.02	87.70
III	0.10	85.44	0.31	0.26	0.03	0.21	<0.01	0.11	0.47	86.83
III	0.01	86.73	0.32	0.28	0.04	0.15	0.01	0.07	0.53	88.13
III	0.001	87.59	1.32	0.55	0.04	0.18	0.01	0.06	0.47	90.22
III	0.0001	98.56	0.79	0.28	0.26	0.68	0.02	0.15	0.43	101.17

[a] Not analyzed. [b] Not detectable.

lowest treatment rates in experiments II and III approached the limit of detection. Therefore, the reliability of the tissue and water concentrations is not as good as for higher treatment rates. However, we feel that sufficient control methods were used and secondary analyses run that the ^{14}C values were correct. Conversely, since the concentration was so low, there is no way to prove that the ^{14}C measured actually was TCDD.

Most (85–99%) of the ^{14}C-TCDD originally added to the ecosystem remained in the soil at the end of the experiment (Table III). Water and algae generally contained the next highest amount of TCDD while other components of the biomass contained substantially smaller quantities. The systems were not exhaustively analyzed to recover all TCDD (losses to adsorption to the tank and suspended particulate matter, and volatilization were not accounted for). Nevertheless, total recovery ranged from 86.8–101.2% and averaged 92.2%, indicating that TCDD was very stable during this study.

We expected that TCDD, adsorbed to soil at very low concentrations, would not go into solution and, therefore, would not be available to aquatic organisms since TCDD is tenaciously adsorbed and immobile in soil (*1*). That accumulation did occur in all organisms from soil containing 0.1 ppb TCDD is important since this concentration approaches that which would occur under normal field use of 2,4,5-T. An application of 2,4,5-T (containing 0.1 ppm TCDD) at the rate of 1 lb/A would result in a soil TCDD concentration of 7.6 and 1.5 ppt in the surface 1- and 5-mm depths, respectively, or about $^1/_{13}$–$^1/_{70}$ of the lowest treatment concentration (0.1 ppb). The same 1 lb of 2,4,5-T applied to an acre-foot of water (1.233×10^6 liters) would result in a concentration of 0.037 ppt TCDD or nearly the same as the lowest water concentration (0.05 ppt) obtained in our ecosystem. These results suggest that under certain circumstances—e.g., discharge of storm runoff from recently treated rangeland into a small pond, water eroded surface soil or debris may contain enough TCDD for measurable (ppt quantities) residues to accumulate in fish or other aquatic organisms. However, TCDD (originating from 2,4,5-T applications) discharged into large lakes, streams, or estuaries would probably become sufficiently diluted so that no measurable accumulation would occur.

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Received for review May 6, 1974. Accepted February 25, 1975.

Operational Characteristics of the Vibrating Orifice Aerosol Generator

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■ A universal scaling parameter has been recognized which allows the researcher to ascertain the monodisperse frequency range of the Vibrating Orifice Aerosol Generator by simply optically sizing the aperture used and selecting a reasonable flow rate. The need for experimentally establishing the correct modulation frequency has been eliminated for two commonly used aperture sizes which allow aerosols in the 0.8–30μ size range to be produced.

In an earlier paper [Wedding, J. B., Stukel, J. J., *Environ. Sci. Technol.*, 8 (5), 456 (1974)], a general relationship was published to allow determination of the correct disturbance wavelength (λ) for production of monodisperse aerosol when applied to a jet of liquid of constant velocity. The expression, given by

$$\frac{Q}{f_{\max} \times A_j \times D_j} \leq \frac{\lambda_{\min,\max}}{D_j} \leq \frac{Q}{f_{\min} \times A_j \times D_j} \qquad (1)$$

still required $f_{\max}$ to be determined experimentally which allowed D_j to be calculated (as $\lambda_{\min}/D_j = \pi$ for $f_{\max}$). Then, by use of plot in the earlier paper, $f_{\min}$ could be determined to establish the overall operating frequency range for monodisperse aerosol. This procedure, which requires considerable experimental effort, would be acceptable except for the fact that tolerances on commercially produced electron microscope beam apertures may be as much as 10%.

The missing element here is a scaling parameter that the ratio D_A/D_j and λ/D_j may be referenced to, enabling one easily to calculate the monodisperse operating frequency for a given aperture size and flow rate without necessitating experimental calibration of each new aperture individually, when a replacement or size change becomes necessary. The best scaling parameter appears to be the jet velocity through the aperture. Figure 1 shows D_A/D_j, λ/D_j plotted vs. V_A. The λ/D_j plots are for two commonly used aperture sizes of 9–10μ and 21–22μ. While the lower limit is π, it is seen that the upper limit varies widely. These plots are not precise and are to serve only as a guide in selecting operating frequencies using Equation 1. The procedure for generating these plots was entirely experimental. It consisted of collecting numerous samples of particles using millipore filter paper of 0.22μ pore size for different aperture flow rates allowing a range of V_A to be established. Each collected sample was individually sized using an optical microscope at 1000X and a Leitz traveling hair (Filar) eyepiece until the monodisperse (σ_g = 1.06) frequency range was established. Then D_j was calculated and the upper and lower bounds for λ were determined for all cases. The particles were made of uranine dye (sold commercially under the name fluorescein) dissolved in water.

The results for the ratio of D_A/D_j are linear and range from about 0.84–0.96 for a velocity range of 700 cm/sec to 2500 cm/sec. With this plot, the maximum operating frequency may be determined using the left-hand side of Equation 1 (where $\lambda_{\min,\max}$ apply to the left- and right-hand side of the inequality, respectively) and the value of

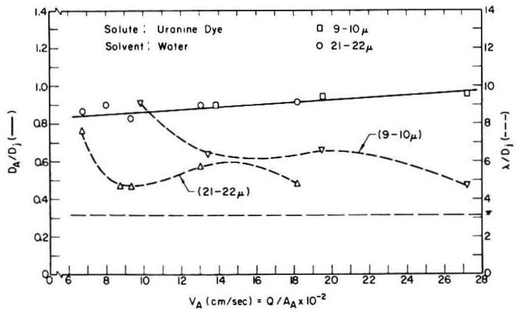

Figure 1. D_A/D_j and λ/D_j vs. V_A for aperture sizes of 9–10μ and 21–22μ

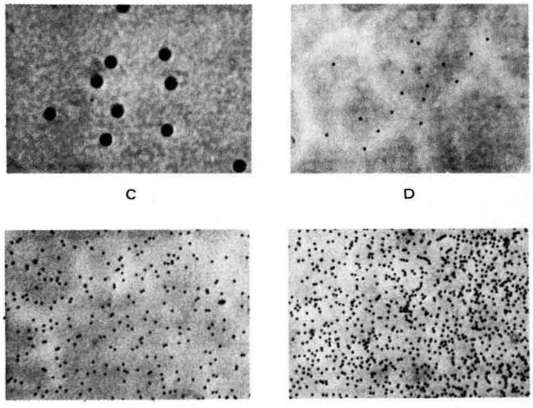

Figure 2. Aerosol quality using uranine and water
A–C. 6.77μ at 640X. D–F. 6.77μ at 160X

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D_A/D_j obtained from the plot for the particular velocity used, again recalling that $\lambda_{min}/D_j = \pi$ and by making the reasonable assumption that $V_A \sim V_j$. Thus, f_{max} is determined without the time-consuming and error-prone experimental calibrating previously required. One must be careful in sizing the aperture, however, and in ensuring a constant velocity through the aperture as by using an infusion pump (good quality one available from Harvard Apparatus, Milas, Mass.).

The upper limit of λ may be approximately determined by the upper dashed curves for λ/D_j and the value just found for D_j. Then the lower limit on disturbance frequency may be calculated by applying the right-hand side of the inequality. Within this overall operation envelope, an optimum frequency will exist at which aerosol quality is best.

An example of Aerosol quality following this procedure is given in Figure 2.

Nomenclature

A_j = area of the jet, = $\pi D_j^2/4$, cm^2
D_A = diameter of aperture, cm
D_j = diameter of the jet, cm
$f_{max,min}$ = monodisperse operating frequency maximum and minimum, respectively
Q = volume flow rate through aperture, cm^3
$V_{A,j}$ = velocity through the aperture, jet, respectively

Greek Letters

λ = disturbance wavelength for monodisperse operation
π = 3.1416 . . .

Received for review October 4, 1974. Accepted February 7, 1975.

Facile Incorporation of Chlorine into Aromatic Systems During Aqueous Chlorination Processes

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■ It has been observed that chlorine is readily incorporated into aromatic compounds under those conditions utilized for water renovation. The extent of chlorine incorporation varies with pH and contact time.

There is a mounting awareness that there may be environmentally deleterious chlorine-containing chemicals (other than chloramines) produced during a water renovation process (*1–7*). The present report deals specifically with the aqueous chlorination of aromatic systems and the examination of the relationship of chlorine incorporation to pH and contact time.

Within the typical ranges of pH found during the course of most water treatment processes (pH 5–9), the active chlorine species could range from entirely hypochlorite ($^-$OCl) to entirely hypochlorous acid (HOCl pK_a = 7.5 at 20°C). It has been observed that chlorine is more readily incorporated into aromatic systems at lower pH values (*8*), a result which parallels the observation of increasing disinfection capability with decreasing pH (*1*). The active chlorinating species has not yet been determined although it is known not to be the Cl^+ ion (*9*).

Monosubstituted aromatics were exposed to low concentrations of aqueous chlorine (7 × 10^{-4} *M*, 20 min, Table I), with the extent of chlorine incorporation following well-recognized trends whereby aromatics containing "activating" groups such as hydroxyl, ether, amine derivatives, or alkyl undergo electrophilic aromatic substitution faster than those containing "deactivating" groups such as nitro, chloro, nitrile, and carbonyl (*10, 11*). Phenol is unique in being readily chlorinated at high pH values in that, although the chlorinating agent is hypochlorite, the substrate is the very reactive phenolate anion.

A detailed analysis of the aqueous chlorination process was also accomplished using biphenyl as the aromatic species. Biphenyl was chosen for study owing to the availability of methodology for isomer recognition and the considerable interest that has recently centered on the possible production of polychlorinated biphenyls (PCBs) at waste treatment facilities known to receive biphenyl (*11*).

Experimental

Typical Procedure (Table I). All reactions were carried out in a 500-ml volumetric flask. To each flask was added 12.72 ml of the 3.84-mg/ml NaOCl solution, HCl (for pH adjustment), and the test solution. The reaction temperature was maintained at 25 ± 0.2°C using a constant temperature bath. A 20-ml aliquot was taken at 20 min and added immediately to a flask containing 15 ml of 0.00543*N* $Na_2S_2O_3$ solution, 5 ml of HOAc, 2 ml of KI (50% aqueous) and 1–2 ml of freshly prepared starch solution. This was titrated to a faint purple color using 0.096 mg/ml of NaOCl solution.

Typical procedure (Table II). To five of the bottles containing 100 ml of distilled water and saturated biphenyl, 100 ppm of $Ca(OCl)_2$ were added, and to another five bottles, 100 ppm of $Ca(OCl)_2$ were added. The remaining five bottles, containing water and biphenyl only, served as con-

Table I

	pH		
	3	7	10.1
(9.5 ± 0.6 × 10^{-4} *M*)	% Cl (uptake)	% Cl	% Cl
Phenol	97.8 ± 0.1	97.6 ± 0.1	97.6 ± 0.2
Anisole	80.7 ± 0.2	11.4 ± 0.4	2.8 ± 0.3
Acetanilide	55.3 ± 0.5	3.4 ± 0.2	—
Toluene	11.1 ± 0.1	2.9 ± 0.4	—
Benzyl alcohol	2.3 ± 0.2	—	—
Benzonitrile	2.1 ± 0.2	—	—
Nitrobenzene	1.8 ± 0.1	—	—
Chlorobenzene	1.8 ± 0.1	—	—
Methyl benzoate	1.8 ± 0.2	—	—
Benzene	1.5 ± 0.1	—	—

Chlorine (7.0 × 10^{-4} *M*), 20 min, 25°C.

Table II

Chlorine source	pH	Chlorine, ppm	Reaction time, hr	Reaction, %	Ppb of chlorinated product 2-	3-,4-	2,2′	2,3′-2,4′	4,4′-
$Ca(OCl)_2$	5.5	100	24	0.4	15	10			
$Ca(OCl)_2$	5.5	100	48	1.0	32	27			
$Ca(OCl)_2$	5.5	100	72	1.7	56	47			
$Ca(OCl)_2$	5.5	100	120	2.5	69	82			
$Ca(OCl)_2$	5.5	10	120	0.004	0.1	0.12			
$Ca(OCl)_2$	5.5	20	120	0.02	0.44	0.51			
$Ca(OCl)_2$	5.5	35	120	0.04	1.4	1.2			
$Ca(OCl)_2$	5.5	50	120	0.15	4.0	4.9			
$Ca(OCl)_2$	5.5	100	120	0.27	8.8	7.4			
Cl_2	2.1	10.9	0.25	2.2	120	10			20
NaOCl	2.8	295	0.25	9.3	450	190	10	130	40
Cl_2	4.9	266	0.25	0.1	5–10				
NaOCl	10.4	830	0.25	0.6	40				
Cl_2[a]	2.2	1350	0.25	16	180	80	80	370	500
NaOCl	7.0	2950	0.25	5.2	280	110		80	30

Saturated biphenyl solution found experimentally to be 6.0 mg/l.
[a] Higher chlorinated isomers also present.

trols. The pH of the final solutions was approximately 5.5. Samples were extracted at intervals of one day, one from each concentration of $Ca(OCl)_2$ and a control, resulting in exposure periods of 1, 2, 3, 4, and 5 days. The entire contents of a bottle was transferred to a 250-ml separatory funnel and extracted three times with 25 ml of hexane. The bottles were rinsed with the first 25-ml aliquot. The combined hexane extracts were filtered through anhydrous sodium sulfate and concentrated in a Kunderna-Danish evaporative concentrator. The hexane concentrates were analyzed with electron capture gas chromatography (EC/GC) using the following conditions.

Analysis Conditions (Samples 1–9). Instrument: Hewlett-Packard 5753A (Ni-63 Electron Capture Detector). Column: 2M × ¼″ glass–4% XE-60 silicone on 80/100 mesh HP Chromosorb W. Injection temperature: 200°C. Column temperature: 130°C isothermal. Detector temperature: 250°C. Carrier: helium @ 60 ml/min. Purge: 10% methane/argon @ 120 ml/min. Pulse interval: 50 μsec.

Analysis Conditions (Samples 10–15). Instrument: Tracor Model 550 Gas Chromatograph (tritium-electron capture detector). Column: 6′ × 4 mm ID glass column—3% $0_v - 7$ on 80/100 HP chromosorb W. Injection temperature: 200°C. Column temperature: 135° or 155°C isothermal. Detector temperature: 210°C. Carrier: nitrogen @ 70 ml/min. Purge: nitrogen @ 30 ml/min.

Compound Identification and Calibration. Chlorinated isomers were designated by comparison with pure materials (as determined by GC-Mass Spec). The percent reaction is based on peak areas as compared to standards and on the experimentally determined solubility of biphenyl (6.0 mg/l.).

The results described in Table II confirm the possibility of chlorine incorporation into the biphenyl nucleus under a variety of aqueous conditions. It should be noted that the extent of chlorobiphenyl production was also found to be dependent on pH such that at values above pH 4 extended reaction times were required to observe extensive chlorine incorporation. It is significant that substantial amounts of higher chlorinated isomers are observed at increased chlorine concentrations if one is considering the potential problems associated with "superchlorination" for such purposes as sludge solubilization.

The possible incorporation of carbon-bound chlorine into the variety of organic materials present in water is important when attempting to evaluate the totality of the environmental impact of the aqueous chlorination process. The ability of the relatively unactivated biphenyl nucleus to be chlorinated under a wide range of aqueous chlorination conditions, plus the facile chlorination of those compounds (phenols and aromatic ethers) that resemble a host of naturally occurring compounds, suggests strongly that we would not be surprised at the apparent discovery of a plethora of chlorinated organics that could be produced in this manner (*3*). These results are particularly significant when it is realized that the chlorinated materials will remain after any subsequent standard reductive process (e.g., SO_2) for chloramine removal. These observations, along with those cited, strongly suggest a reevaluation of chlorination in water bearing high organic content.

Acknowledgments

The authors wish to acknowledge the major contribution of H. Weingarten, S. Tucker, and W. Mees, Monsanto Co., St. Louis, Mo. 63166, in providing a significant portion of the data contained in Chart II (i.e., samples 1–9). Standardized samples of chlorinated biphenyls were provided by Gary Glass, National Water Quality Laboratory, Duluth, Minn., and Ronald G. Webb, Southeast Water Laboratory, EPA, Athens, Ga.

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Received for review November 15, 1974. Accepted March 21, 1975.

Oxidation of Cinnabar by Fe(III) in Acid Mine Waters

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■ Fe(III) concentrations occurring in acid mine drainage water oxidized cinnabar (HgS), the most common natural mercury mineral. With Cl^- present at environmental levels, significant mercury was released to solution. The rate of oxidation of cinnabar was much higher than the rate of mercury release to solution. Most of the mercury was bound to the remaining cinnabar by an unknown mechanism. An isotopic dilution technique was used to calculate the total mercury, both in solution and bound to the remaining cinnabar, released by oxidation.

The average concentration of mercury in the earth's crust is about 80 ppb, but levels more than 10,000 times higher are found in mineable natural deposits occurring in regions of intense tectonic activity (*1*). Mercury release from these natural sources may have been occurring throughout geologic time and may be aggravated by mining. The most common mercury-bearing minerals occurring in these deposits are cinnabar and metacinnabar, both isomorphs of HgS. Compared to most sulfides, they are very insoluble (*2*) and appear more resistant to oxidation (*3*).

Saukov and Aidinyan (*4*) reported that cinnabar could be oxidized by solutions containing 20–162 mM Fe(III). Chloride (0.2*M*) increased the oxidation rate 14 times as inferred from observed reduction of Fe(III) to Fe(II). Measured mercury in solution averaged only about 1/300 the concentration expected on the basis of the concentration of Fe(II) formed, and they concluded that the mercury released was removed from solution as $HgSO_4{\cdot}2HgO$. Fe(III) and Cl^- occur in acid drainage waters from mining areas, but in lower concentrations than investigated by Saukov and Aidinyan. We wished to determine whether cinnabar oxidation might occur under these environmentally significant conditions.

Procedures

Cinnabar was prepared from a sample of recently mined, high-grade ore from the New Almaden mine, Santa Clara County, Calif. The ore was crushed and sieved to obtain the −325 +400 mesh (Tyler series) fraction. Cinnabar was hydraulically separated from other ore components, washed with 50% nitric acid to remove traces of pyrite, then reground in a porcelain ball mill to minimize the amount of surface area possibly altered by the nitric acid treatment. The surface area of the resulting material was 1.08 m^2/g as determined by B.E.T. nitrogen adsorption.

A small acid (pH 2.0) stream from a tailings pile near an abandoned mercury mine at Mt. Diablo, Calif. was analyzed to obtain some idea of reasonable initial Fe(III) and Cl^- concentrations. It contained 4 g/l. (72 mM) total iron and 250 mg/l. (7 mM) Cl^-. Titration with permanganate indicated that at least 3/4 of the total iron was Fe(III). Total iron was measured by atomic absorption and chloride by argentometric and mercuric nitrate methods. The soluble mercury concentration in the stream, measured by flameless atomic absorption (FAA), was 20 ppb (0.1 μM).

The effect of Fe(III) and Cl^- concentrations on cinnabar oxidation by Fe(III) and mercury release to solution were evaluated using Pyrex centrifuge tubes with Teflon-lined plastic caps. Tubes containing cinnabar, the oxidizing solution, and a gas phase were mounted in racks on a shaking table at 25°C. Fe(III) was added as the perchlorate salt, and Cl^- as NaCl. The pH was adjusted with perchloric acid to prevent Fe(III) hydrolysis and to duplicate the low pH conditions in acid drainage waters.

Mercury released to solution was determined by FAA analysis of the filtrate from 0.45-μ Millipore filters. The gas phase was sampled prior to opening the tubes and analyzed by FAA; no elemental mercury was found. Losses to the container walls, as monitored by recovery of $^{203}Hg(II)$ added to samples without cinnabar and by mercury analysis of nitric acid washes from emptied tubes, proved insignificant. A NaI crystal scintillation counter determined $^{203}Hg(II)$ concentrations. Losses to Millipore filters were significant only at very low mercury concentrations.

Early experiments indicated that much of the mercury released by cinnabar oxidation became bound to the remaining cinnabar. To distinguish this mercury from that present as cinnabar (cinnabar-Hg) and that dissolved in the aqueous phase, we will refer to it as "bound-Hg." It was possible to differentiate between bound-Hg and cinnabar-Hg by adding a pool of $^{203}Hg(II)$ tracer to the cinnabar–solution mixture of an oxidation experiment. Cinnabar-Hg does not exchange with the $^{203}Hg(II)$ pool, while bound-Hg does exchange. This exchange dilutes the specific activity of the tracer pool, permitting calculation of the quantity of bound-Hg present.

Proof that added tracer exchanges with only the bound-Hg was obtained as follows: $^{203}Hg(II)$ was placed in a nonoxidizing solution containing HgS. The total Hg(II) concentration added with the tracer was only 20 ppb, and over 98% of the tracer was removed from solution by the HgS. Next, a much larger concentration (33 mg/l.) of unlabeled Hg(II) was added. Within 3 hr the distribution of tracer between solids and solution was the same as the distribution of the total Hg(II) added (65% in solution). The amount of Hg(II) and tracer in solution remained constant (for 45 days) indicating that ^{203}Hg was not exchanging with mercury in the HgS crystal. In oxidation experiments results were essentially the same when tracer was added either prior to or after oxidation, giving further evidence of free exchange between bound-Hg and mercury in solution.

Results

Figure 1 illustrates the rate of release of soluble mercury from New Almaden cinnabar exposed to Fe(III) and Cl^-. The system containing both Fe(III) and Cl^- gave rates of mercury release to solution more than an order of magnitude greater than a similar system without Fe(III), and two orders of magnitude greater than a system with Fe(III) but no Cl$^-$.

Figure 2 illustrates the mercury released to solution from New Almaden cinnabar using a range of Cl$^-$ concentrations and 10 mM Fe(III). The amount released was strongly affected by Cl$^-$ concentration.

Figure 3 illustrates the rates of mercury release to solution as a function of cinnabar concentration. Contrary to original expectations, larger concentrations of cinnabar released less mercury to solution. Small amounts of Hg(II) (20 ppb) containing ^{203}Hg at high specific activity were added to these samples to confirm the presence of bound-Hg and estimate its quantity, thus allowing calculation of the true cinnabar oxidation rate. The results are shown in Figure 4. Larger concentrations of cinnabar result in greater calculated oxidation rates. The calculated amounts re-

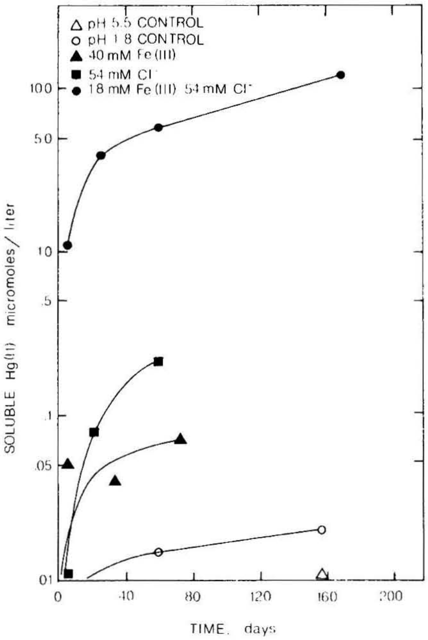

Figure 1. Effect of Fe(III) and Cl$^-$ on release of soluble mercury from New Almaden cinnabar oxidation in systems with 3 g/l. HgS and pH between 1.8 and 2.0

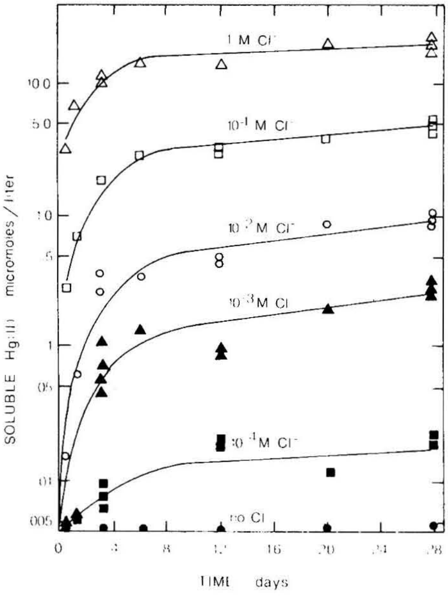

Figure 2. Effect of varying Cl$^-$ concentration on release of soluble mercury from 2 g/l. New Almaden cinnabar in systems containing 10 mM Fe(III) at pH 1.5

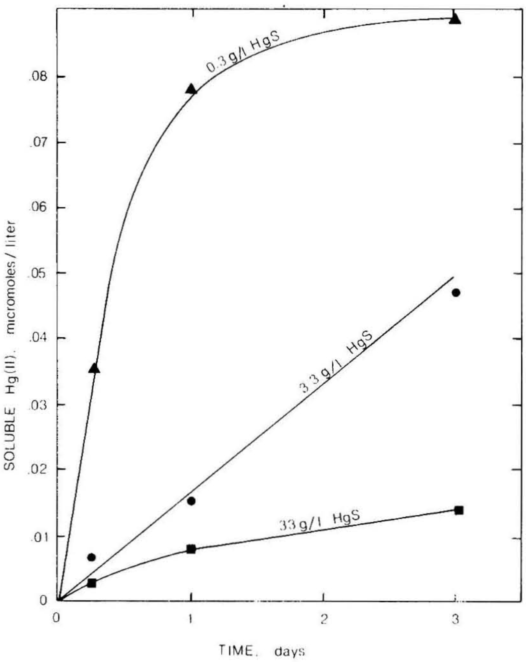

Figure 3. Effect of varied New Almaden cinnabar concentrations on release of soluble mercury in pH 1.5 solutions containing 10 mM Fe(III) and 7 mM Cl$^-$

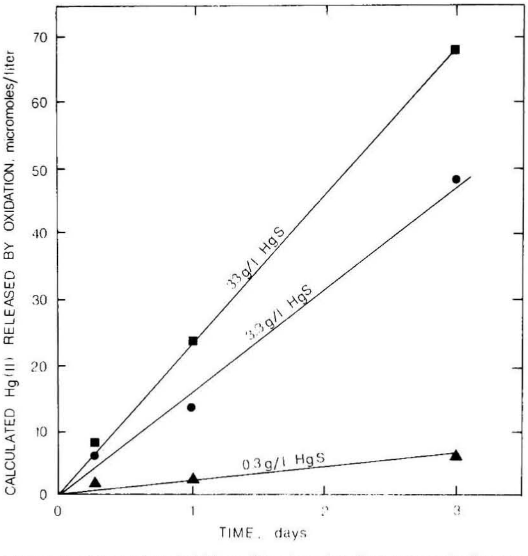

Figure 4. Effect of varied New Almaden cinnabar concentrations on calculated oxidation rate. Experimental conditions are the same as for Figure 3

leased by oxidation were several orders of magnitude greater than the measured amounts in solution. Controls in which no tracer was added gave the same mercury release to solution, indicating that Hg(II) added with the tracer had little effect on oxidation or the partition between solution and bound-Hg. Evidently, the large amount of bound-Hg made a 20-ppb addition insignificant.

Discussion

These laboratory studies indicated that significant rates of oxidation of cinnabar and release of mercury to solution can occur under conditions prevalent in acid mine drainage waters.

Other studies in our laboratory have shown that Hg(II) is strongly adsorbed by HgS, and that, in the process, anions such as SO_4^{2-}, NO_3^-, and Cl^- may also be removed from solution. Since mercury released by oxidation is largely held on the remaining cinnabar, the oxidation rate cannot be directly inferred from mercury released to solution. Larger concentrations of cinnabar increase not only the surface area available for oxidation but also that available for removal of Hg(II) released by oxidation. The results illustrated in Figures 3 and 4 can be explained if the effect from increasing surface area was greater on Hg(II) removal than on oxidation.

Additional work is needed to identify the nature of the bound-Hg. Studies are continuing on this problem and on the kinetics of cinnabar oxidation over a range of pertinent variables broader than those in acid drainage environments.

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Received for review Aug 29, 1974. Accepted February 13, 1975. This work was supported by the National Science Foundation through the Trace Contaminants Program of the RANN Division, Grants GI-32943 and 40614.

Interference of Sulfate Ion on SPADNS Colorimetric Determination of Fluoride in Wastewaters

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■ Serious errors have been experienced in the analysis of wastewater samples for fluoride concentration by the SPADNS colorimetric method. The source of positive interference in this method was due primarily to sulfate ion carry-over during the preliminary distillation step.

In accordance with the Federal Water Pollution Control Act Amendments of 1972, the October 16, 1973, *Federal Register* (*1*) specifies the approved test procedures for the analysis of water pollutants. The approved method for the determination of fluoride ion is the SPADNS colorimetric procedure preceded by distillation from a sulfuric acid solution. The SPADNS method and the fluoride electrode method we had been using are both described in detail in Standard Methods (*2*) and Part 23 of ASTM Annual Book of Standards (*3*).

In the process of adopting the SPADNS method for routine laboratory use, comparative data were gathered on prepared standard fluoride solutions and actual wastewater samples using both methods. The data showed that after sample distillation, the SPADNS method gave consistently higher results than the electrode method. A study was initiated to discover the source and extent of the apparent interference. Since it had previously been reported that at the 1.0-mg/l. fluoride level, 200 mg/l. of sulfate ion will cause a positive error of 0.1 mg/l. in the SPADNS results (*2, 3*), the study was concentrated on sulfate ion. This appeared to be a logical beginning because of the possibility of sulfate carry-over during distillation.

Methodology

The colorimetric procedure is based upon the measurement of the loss of color of a zirconium-dye lake owing to the reaction of fluoride ion with zirconium to form a colorless complex ion. The dye used is sodium 2-(*p*-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate (SPADNS). The range of the test is 0.1–1.4 mg/l. of fluoride. The method is subject to many interferences, most of which are supposed to be eliminated by the preliminary distillation step.

The distillation procedure was first proposed by Bellack (*4*) in 1958. It involves the distillation of 300 ml of sample from a water solution of sulfuric acid which has previously been heated to 180°C and cooled. Distillation is continued until the temperature reaches 180°C and approximately 300 ml of distillate have been collected. This procedure is supposed to assure complete recovery of up to 3 mg/l. of fluoride ion and removal of most of the interfering constituents in the water sample. Sulfate carry-over is reported to be minimal as long as the temperature in the distillation flask does not exceed 180°C.

The electrode method requires the use of a fluoride ion selective electrode, a calomel reference electrode, and a pH meter with an expanded millivolt scale. A buffer solution is added to a portion of the raw sample or preferably to the distillate to adjust pH, to complex iron and aluminum which would interfere, and to provide a similar ionic strength background between samples and standards. The fluoride electrode develops a potential which is specific for fluoride ion and is proportional to the fluoride ion activity of the sample. The range of this method is 0.1–1000 mg/l. fluoride.

Experimental

Excellent comparative data were obtained when the two methods were used to analyze undistilled prepared standard fluoride solutions in the range 0.0–1.4 mg/l. Marked differences were found, however, when actual wastewater samples were analyzed following distillation. The results obtained by colorimetric analysis were in all cases higher

Table I. Results of Analysis of Wastewater Samples Following Distillation

Sample identification	SO_4^{-2}, mg/l.	Electrode, mg/l. F	SPADNS, mg/l. F^-
Distilled water	400	<0.1	0.4
Distilled water	1300	<0.1	0.7
Mining operation—well water	475	1.6	2.1
Mining operation—well water	800	1.5	2.1
Mining operation—well water	285	1.3	1.6
Mining operation—well water	990	1.0	1.9
Mining operation—well water	430	1.2	1.8
Power plant—river water	95	<0.1	0.1
Power plant—ash basin	100	0.1	0.2
Power plant—circulating water	1140	<0.1	0.6
Power plant—sewage	340	0.2	0.5
Power plant—floor drains	150	0.3	0.4
Power plant—screen wash	200	<0.1	0.2
Power plant—cooling tower water	1150	0.2	0.8
Mining operation—well water	500	0.6	1.5
Mining operation—well water	330	1.9	2.1
Steel mill—thermal	340	0.3	0.5
Steel mill—main	265	0.2	0.4
Steel mill—river	210	0.2	0.3
Power plant—river	95	0.1	0.2
Power plant—septic tank	1185	0.1	0.6
Power plant—discharge	180	0.2	0.3

than results obtained with the electrode method. In most cases the difference was greater than 100%.

To determine if sulfate carry-over was occurring and to what extent it would interefere in the SPADNS method, another series of 22 samples was analyzed by both methods. Prior to measurement of the fluoride concentration, a portion of each distillate was analyzed for sulfate ion concentration. The results presented in Table I show an average sulfate concentration of 500 mg/l. with a range 95–1300 mg/l. Analysis of the data suggests a direct relationship between the positive error in the SPADNS method and the sulfate ion concentration of the distillate.

To determine the effect of various levels of sulfate concentration, a series of fluoride standards containing 0–1600 mg/l. of sulfate were analyzed by both methods. The results shown in Table II indicate that the effect of sulfate is greatest in the low fluoride range. At the 1-mg/l. fluoride level, the average error is about 20%. Much greater differences were found on actual sample analysis as shown in Table I which indicates that other factors are involved. The data indicate that correction factors or standard addition of sulfate is not a practical solution to the problem.

Table II. Results of Analysis of Prepared Standards Containing Various Concentrations of Sulfate

F^- added, mg/l.	SO_4^{-2} added, mg/l.	Electrode, mg/l. F	SPADNS, mg/l. F
0	0	<0.1	<0.1
0	200	<0.1	0.1
0	400	<0.1	0.3
0	800	<0.1	0.5
0	1200	<0.1	0.6
0	1600	<0.1	0.7
0.1	0	0.1	0.1
0.1	200	0.1	0.2
0.1	400	0.1	0.3
0.1	800	0.1	0.4
0.1	1200	0.1	0.6
0.1	1600	0.1	0.8
0.5	0	0.5	0.5
0.5	200	0.5	0.6
0.5	400	0.5	0.7
0.5	800	0.5	0.8
0.5	1200	0.5	0.9
0.5	1600	0.5	1.0
1.0	0	1.0	0.9
1.0	200	1.0	1.1
1.0	400	1.0	1.2
1.0	800	1.0	1.2
1.0	1200	1.0	1.3
1.0	1600	1.0	1.3

Conclusions

All of the available methods for the determination of fluoride in wastewaters require distillation to eliminate interferences and to assure recovery of all forms of fluoride. We have demonstrated, however, that sulfate carry-over during distillation is considerable. Since sulfate ion causes a large positive error in the SPADNS colorimetric method, we suggest that the fluoride ion electrode method following distillation be adopted as the method of choice.

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Received for review June 19, 1974. Accepted January 16, 1975.

INDUSTRY TRENDS

Dames & Moore (Los Angeles, Calif.) says that its volume has grown to over $65 million, an increase of about 40% over the previous year, despite a slow economy.

American Air Filter Co., Inc., is supplying 84 electronic air cleaners to John Deere & Co., to remove welding fumes and airborne particulates.

Willis & Paul, Inc. (Netcong, N.J.) will furnish three ACFM venturi-type air scrubbers to Floridin Co., to clean exhaust air from three Fuller's earth dryers at Quincy, Fla.

Betz introduced **Betz Energy Engineering** with a view to helping the hydrocarbon processing industry develop more meaningful energy conservation programs.

The Rust Engineering Co. will do detailed engineering for a 900 tpd recovery boiler and a 15,000 kW turbine generator for The Chesapeake Corp. of Virginia.

Universal Oil Product Company's ROGA Division announced that the first major commercial reverse osmosis system, which it built, is now on-stream near Ramona, Calif. The unit handles 250,000 gpd.

The Electric Power Research Institute (Palo Alto, Calif.) will sponsor a $306,000 nuclear power plant safety research project with Stanford Research Institute to examine strength of reinforced concrete impacted by debris during a tornado.

Eastman Kodak (Rochester, N.Y.) is building an innovative $9 million facility to burn waste chemicals. Start-up is expected in early 1976. Only a scrubbed white plume will be seen.

Brown Boveri AG (Baden, Switzerland) received an order to design and build 18 main field coils for controlled hydrogen fusion research from the Max Planck Institute (Garching, West Germany).

Carus Chemical Co. has completed pilot-plant evaluation of a new odor control process that uses the company's catalyst, which is made with potassium permanganate.

Stanmar, Inc. (Sudbury, Mass.) plans to custom design and build a private residence utilizing an advanced solar energy system. The experimental home is being built by Raytheon, and will use a high-efficiency heat pump.

Husky Industries (Atlanta, Ga.) will expand its 10 million-lb capacity powdered activated carbon plant by nearly 100%.

PPG Industries will market a water-based varnish that can reduce hydrocarbon emissions, such as mineral spirits or turpentine vapors.

Environmental Devices Corp. (ENDECO) has developed an improved system for detecting heavy metals, including toxic ones, in municipal water supplies, some down to 5 ppb.

Blyth Eastman Dillion & Co. (New York City) and Salomon Brothers negotiated the purchase of $15 million of pollution control revenue bonds for the County of Sweetwater, Wyo.

Combustion Equipment Associates will supply a 450 MW flue gas desulfurization system for about $17 million for the Square Butte Electric Cooperative near Bismarck, N.D.

Charles Yulish Associates, Inc. (New York, N.Y.) is offering a new "Threat Analysis and Protection Service" with regard to nuclear facility safety from attempted employee sabotage.

The Monsanto Enviro-Chem processes will be used in two sulfuric acid plants to be built by **Simon-Carves Africa** (Johannesburg, South Africa) for Triomf Fertilizers Ltd., at Richards Bay. Cost is $16 million. Clean air standards will be met.

BIF, a unit of **General Signal,** is adding a computer system equipment line to interface with BIF's supervisory control instrumentation for water and wastewater processes.

Sappi Ltd. (Johannesburg, South Africa) contracted with the Copeland Group of companies for a new chemical recovery plant, to replace an existing kraft recovery plant and solve air and water pollution problems. Cost is about $5 million.

Dravo Corporation's Water and Waste Treatment Division has licensed Fuji Electric Co., Ltd. (Tokyo, Japan) to design, build, and manufacture Dravo's Denite System for wastewater treatment in Japan.

Connell Associates, Inc., of Florida, has become Connell/Metcalf & Eddy, Inc. Both Connell and Metcalf & Eddy are part of the Environmental Engineering group of Research-Cottrell, Inc.

Proler International Corp. (Houston, Tex.) will build two hot-process steel briquetting plants, to turn 10,000 t/month of contaminated turnings and borings into clean steel briquettes, for about $4 million.

Waste Management, Inc. (Oak Brook, Ill.) has received a $15 million, 5-yr contract from Garrett Research and Development Co. for subsystems operations at the 450,000-t/yr energy and resource recovery facility, Bridgeport, Conn.

American Air Filter Co., Inc. has a $4.4 million order from Armco Steel Corp. for a fabric collector system to control emissions from two 150-ton electric arc furnaces at Armco's new Kansas City, Mo., facility.

Swemco Inc. (New York, N.Y.) has received a $250,000 flue-gas scrubber contract, to remove SO_2 from two 300,000-lb/hr coal-fired boilers, from Texasgulf, Inc.

The Power Systems Group of **Combustion Engineering, Inc.,** will provide Procon Inc., a division of UOP, with two boilers (220,500 lbs/hr of steam each) to be installed at the Chinese Petroleum Corp.'s Lin Yuan Refinery, Taiwan, Republic of China.

Combustion Equipment Associates, Inc. has been awarded a contract, ultimately worth $17 million, by Sanderson & Porter, Inc., on behalf of Square Butte Electric Cooperative (N.D.) to supply a 450-MW flue-gas desulfurization system.

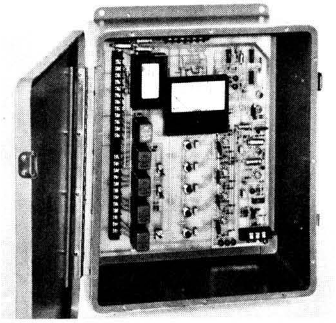
Stanley Consultants, Inc. has received the 1975 Engineering Excellence Award from the American Consulting Engineers Council for the design of an "Air Pollution Abatement System" in operation at Union Carbide Corp., Alloy, W.Va.

Roy F. Weston, Inc. recently participated in the transportation and construction of a 130-ft steel stack for rehabilitating and renovating Solid Waste Incinerator No. 4 of the City of Baltimore (Md.). This construction used the world's largest mobile crane.

Marine Construction and Design Co. (Seattle, Wash.) is supplying the U.S. Navy with two dozen 36-ft aluminum catamaran-hull skimmers for oil spill recovery.

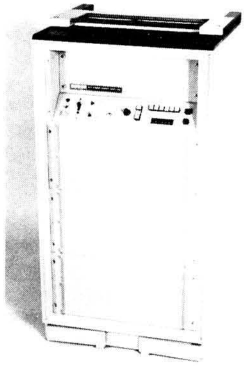
Salem Corp. (Pittsburgh, Pa.), among whose products are anti-pollution facilities, announced that a large West European firm is interested in buying Salem's authorized and unissued stock, not to exceed 25% of the shares then to be outstanding.

NEW PRODUCTS



Liquid level monitor
Indicates and controls level in pump stations and water storage tanks. Features include high- and low-level alarms; setpoints adjustable over the complete range; level, status and alarm signals for telemetry; and the ability to alternate pumps to equalize usage. Universal Engineered Systems, Inc. **101**

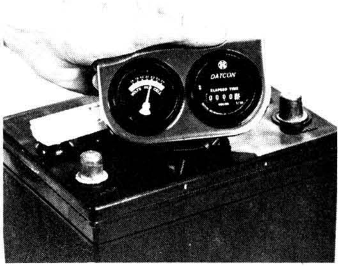
Submersible pumps
Recessed impeller, on-clog pumps are able to handle fresh, waste, effluent and sewage water as well as slurry and sludge. Depending on the model, the pumps will pass from 2–3.25 in. solids, have capacities ranging from 250–1000 gpm, and heads from 20–140 ft. Weil-McLain Company, Inc. **102**



Facsimile scanner
Designed to transmit graphics, alphanumerics, weather charts and picture information at standard network speeds of 120 or 240 scans/min, 48 or 96 lines/in. The scanner's normal mode is an amplitude-modulated double sideband signal. Alden Electronic & Impulse Recording Equipment Company, Inc. **103**

Flexible metallic ducts
Insulated, flexible ducts may be utilized to combat air pollution. Ducts offer noncombustibility, clean surface and easy installation. Clevepak Corp. **104**

Sludge incinerator
Reduces physical-chemical and activated sludges, galley and laundry wastes and concentrated sewage to inert ash. A single incinerator can handle up to 30 gal/hr of sludge with solids content up to 6%. General Electric Co. **105**

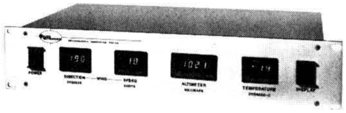


Electric vehicle battery minder
System correlates time and voltage to voltage-drop-per hour rate, which can aid the vehicle operator in preserving battery life. The system was designed for electric fleets where the route length, terrain and load vary from vehicle to vehicle. Datcon Instrument Co. **106**

Level sounder flow computer
System measures open channel flow over weirs and flumes. The ultrasonic flowmeter can be installed without complex electronic test equipment. The transducer's design optimizes signal to noise, while the flow computer offers external outputs, flow proportional sampler control and ac and dc operation. Manning Environmental Corp. **107**

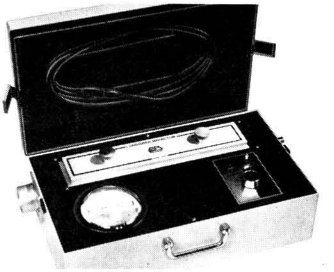
Miniature accelerometer
Measures acceleration, vibration and shock and is capable of withstanding a 1000% overrange at any frequency. Applications include industrial vibration monitoring, animal studies and automotive crash and barrier testing. Entran Devices, Inc. **108**

Noncorrosive scrubber
Three-layer venturi scrubber constructed of steel, polyester flake lining and silicon carbide brick is designed to resist abrasion and acidic conditions. The externally accessible adjustable throat permits the scrubber to operate at varying steam loads. Air Pollution Industries, Inc. **125**



Meteorological observation station
Solid-state, plug-in modules with digital readout are designed for console mounting and continuous displays. Sensors monitor wind, temperature and other meteorological parameters at environmental monitoring stations, weather bureau stations and airport towers. Silver Instruments **109**

Air quality monitoring system
Includes a minicomputer, central station with nine track tape system, line printer, teletype and CRT display, and remote sensor terminals, each capable of accepting inputs from up to 16 instruments. New software includes special summary reports. Signaling pollution alert levels and maintaining or printing records to EPA are system capabilities. Receptors, Inc. **110**



Impactor
Provides particle size distribution as a function of time. Four rotating drums sample at a rate of 3–5 cfm; nominal size cutoffs for each drum are 10, 3, 1 and 0.3 μ. Continuous sampling of liquid or solid particles for up to 24 hr is possible. Sierra Instruments, Inc. **111**

Baghouse pulse control
Timer has digital set point of pulse times from 0.01–99.99 sec for more accurate control of pulsing cycles in reverse pulse baghouses. Standard Havens, Inc. **112**

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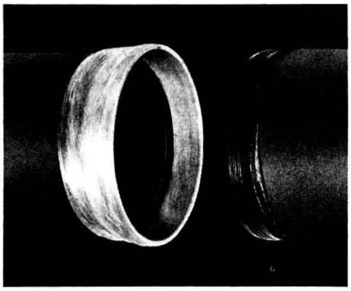
Heating system
Originally developed for nuclear fuel containers, the fiberglass molds can be made to suit the requirements of the power industries and in water treatment and food processing. The mold of the containers are used to fashion thermostatically controlled systems by using fiberglass heating panels. Cooperheat **113**

Automatic liquid sampler
More than 30 influent and effluent models including composite, multiple bottle, proportional to flow and explosion-proof units meet EPA regulations. The user can control sample size and frequency. Most models are portable. Sigmamotor, Inc. **120**



Clay pipe with fiberglass socket
Clay pipe consisting of a fiberglass/polyester socket and urethane spigot joint system makes for lower labor costs because of faster sewer installations. Sockets are resistant to weathering, acid, alkali and gases. The pipe is constructed in 8 in. diameter, 5.5 ft lengths, but other sizes are contemplated. U.S. Concrete Pipe Co. **121**

Pesticide protection system
NIOSH-approved pesticide system removes airborne particulates and pesticide vapors; the air purifier unit supplies clean filtered air to the pesticide handler via tubing to the helmet or hood. 3M Company **122**

Fume abatement process
Removes noxious nitrogen oxide gases from effluent gases in chemical plants. The process can limit NO_x gases to 150 ppm or less on a continuous basis. Goodpasture, Inc. **123**

Heavy metals sensor
When exposed to water, the membrane sandwich sensor adsorbs the metals. The sensor is returned to the company for analysis and the customer is sent a computer printout of the results. Metals concentrations can be read from 1–1000 ppb. Environmental Devices Corp. **124**

Circular chart recorder
Inkless, null balance, servo recorder is designed to record chlorine residual, chlorine gas flow and other variables in industrial and municipal applications. Capital Controls Co. **127**

When EPA comes a-callin' will you be ready?

It's really just a matter of time.

One by one, the EPA and state regulatory agencies are issuing permits for governing discharges into the nation's waters for every industry classification.

Companies whose discharges meet the limitations in their permit will not be affected. Others unquestionably will find themselves facing a difficult decision, i.e. spend money or sacrifice productivity to meet the requirements—or shut down.

Take heart. The EPA is reasonable. They'll listen to documented facts. And, if the facts warrant, we believe they will adjust their requirements.

For example, your plant may not be the source of pollution in your area. Under these circumstances, give the EPA objective documentation which shows the characteristics of your effluent demonstrate this fact.

The guideline for your industry may contain "textbook specifications". In such a case, you may be helped in negotiating your permit if you give the EPA documentation which shows that these specifications are more stringent than necessary.

One thing is certain. The EPA will require objective documentation—not words.

If you have the documentation when it's needed, they'll listen. If you don't, your abatement costs may be unnecessarily high.

If you anticipate—begin to get the documentation now—you may save many thousands of dollars later on in shutdowns, legal fees, penalties, fines, "crash" evaluations, etc.

We can help. Aquatic Environmental Sciences is a service organization at Union Carbide—in business to help you define, analyze and objectively document the environmental effects of your effluents.

If you face a problem *now*—or anticipate one in the future, call us. Our experienced, professional staff will discuss the kind of documentation you'll need, how we'd go about developing it, and develop it for you at a reasonable cost.

After we've developed the documentation, it may prove you do have a problem. At the very least you will know how much corrective action will be needed.

On the other hand, you may find that very few modifications, if any, of your plant operations or the way you are treating your discharges will be required.

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CIRCLE 19 ON READER SERVICE CARD

NEW LITERATURE

Fabric collector. Bulletin DC-301C describes a new pulse jet fabric collector and gives full specifications. Dust Control Products, American Air Filter Co., Inc. **151**

Aquatic environmental services. Brochures describe a wide range of company's services in this field. Union Carbide **152**

"Water Pollution Solutions". Ten-page brochure identifies the problem and solution, and explains how the company's OXY FLO high-speed floating aerator, with models up to 100 hp, solves the problem with trouble-free performance. Richards of Rockford, Inc. **153**

Sorbent products. Brochure describes sorbent products specially treated to absorb 15–20 times their weight in oil, and yet resist water. Conwed Corp. **154**

Infrared analyzers. MIRAN I Systems brochure describes a system of infrared analyzers and accessories for a wide variety of applications. Wilks Scientific Corp. **155**

Stream gauging. Bulletin 18 describes stream gauging accessories such as staff gauges, sounding reels, float gauges, tag line and cable hanger connectors, and hook and point gauges. Leupold & Stevens, Inc. **156**

"The Hydromike." Newsletter, published quarterly, is aimed at individuals interested in water resources products applications. Many practical subjects are discussed. Leupold & Stevens, Inc. **157**

Dust collectors. Pamphlet describes the company's line of industrial dust collectors that work by cyclonic flow and impingement, and capture submicron size particles. Alcar Metals, Inc. **158**

Laboratory products. Catalog describes products that protect against biological contamination, extract samples, and perform other tasks in molecular biology and immunology. Spectroderm International, Inc. **159**

OSHA products. Illustrated brochure describes products from the company's OSHA products department. Products for many different industrial and mining situations are listed. 3M Co. **160**

Air quality control. Two brochures concern themselves with electrostatic precipitators and mechanical collectors, and cover the subjects in depth. Emission Control Div., Envirotech **161**

Scrubbers. Brochure is a guide to a complete line of wet scrubbers, absorption equipment, systems, and accessories. Emission Control Division-Envirotech Corp. **162**

Water/wastewater analysis. Catalog lists laboratory reagents and glassware for water/wastewater analysis, including some 70 water and pollution tests. Hach Chemical Co. **163**

Wastewater treatment. Bulletin describes new biological concept for primary, secondary, and tertiary treatment in one continuous operation, to meet effluent standards. ACTIVOX Inc. **164**

Draft control. Manual provides basic and detailed engineering and application data for barometric draft controls, draft inducers, duct boosters, and chimney top draft inducer units. CONCO, Inc. **165**

Fabric filters. Brochure describes the company's line of fabric filters for air quality control and product recovery. Emission Control Division, Envirotech Corp. **166**

Temperature alarm. Bulletin No. 124A fully describes temperature alarm that warns of, and can act against, out-of-tolerance temperature conditions in environmental test chambers. Tenney Engineering, Inc. **167**

Demineralized water. "OSMO Pure Water" brochure describes the firm's newest reverse osmosis equipment, and discusses new USP standards for "Water for Injection" by using reverse osmosis. Osmonics, Inc. **168**

Coal tar epoxy coating. Product Bulletin 701 describes "Flaketar", a newly formulated coal tar epoxy protective coating. The Ceilcote Co. **169**

Aerator motors. Brochure GEA 91678 describes aerator motors used in the accelerating fight to control water pollution. General Electric Co. **170**

Monitoring. Newsletter features diverse applications of continuous infrared monitoring for chemical process analysis, carbon adsorption bed breakthrough, leak detection, and other tasks. Wilks Scientific Corp. **171**

Water protection. Catalog W1855A describes the Metatronic 2000 line of instrumentation, including controllers, recorders, and other equipment for monitoring water and wastewater. Acco **172**

Air pollution control. Company is offering a new "Basic Handbook of Air Pollution Control Equipment" with complete information. Western Precipitation Division, Joy Manufacturing Co. **173**

Purifier. Report No. G-137 discusses the Hydrox purifier, which removes oxygen and water from other gases, such as nitrogen, inert gases, and methane-argon mixtures efficiently. Matheson Gas Products. **174**

Total flow meters. Bulletin 28, 8th Edition, describes Model 61 total flow meters and their accessories. Leupold & Stevens, Inc. **175**

Consulting services. Consulting services in the fields of environmental and polymer sciences are described. H.M. Mittelhauser Corp. **176**

Reverse osmosis. Brochure PB424 describes a wall-mounted reverse osmosis system operable at low cost. Millipore Corp. **177**

Valves. Bulletin WW-100-A describes the company's complete line of wastewater valves. Complete specifications are given. G-A Industries Inc. **178**

Water still. Flyer describes a completely automatic, self-contained water still that can provide up to 5.3 liters/hr of ultra-pure water. Price is under $500. Wheaton Instruments **179**

"Positive Alternatives for Solving America's Litter & Solid Waste Problems". Discusses negative deposits, non-refillable beverage containers, and recycling. Director of Information, Reynolds Aluminum, Richmond, Va. 23261 (write direct).

Environmental impact statements. List of statements on which the EPA commented during March 1975 is now available. EPA Press Office, Room 335, West Tower, 401 M St., S.W., Washington, D.C. 20460 (write direct).

"Representativeness of Watershed Precipitation Samples". Water Research Institute, West Virginia University, Morgantown, W.Va. 26506 (write direct).

"Oil Spills and Spills of Hazardous Substances". Updated edition. Oil and Special Materials Control Division, Office of Water Program Operations, Environmental Protection Agency, Washington, D.C. 20460 (write direct).

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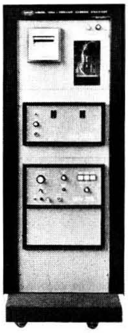

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CIRCLE 2 ON READER SERVICE CARD

BOOKS

Plastics Waste Management. 126 pages. Manufacturing Chemists Association, 1825 Connecticut Avenue, N.W., Washington, D.C. 20009. 1974. $5.75, paper (two-page separate summary free).

This study considers current disposal methods for plastics in the solid waste stream. It looks at incineration, recycle/reuse, pyrolysis, and sanitary landfill. Environmental degradation is also discussed, as is regulatory activity by various states. There is a prediction that U.S. use of plastics will be 60 billion lbs/yr by 1980. DeBell & Richardson, Inc. (Enfield, Conn.) prepared the study for MCA.

Current Advances in Ecological Sciences. Paul Jarvis and Harry Smith, Eds. 160 pages. Pergamon Press Ltd., Headington Hall, Oxford 0X3 0BW, England. Periodical. $100/yr., with reduced rates in special cases.

This periodical provides a monthly current awareness service for biologists, ecologists, and environmental scientists trying to "keep up" with the ever-growing volume of information, books, and journals in their fields. U.S. address is: Pergamon Press, Inc., Maxwell House, Fairview Park, Elmsford, N.Y. 10523.

Solar Energy Home Design in Four Climates. 200 pages. Total Environmental Action, Church Hill, Harrisville, N.H. 03450. 1975. $12.75, paper (postpaid).

Design requirements for solar-heated homes will differ as climate differs. The design useful for, say, Phoenix, Ariz., might not be as workable in Minneapolis, Minn. This book gives detailed designs and explanations for solar-heated home design for a "temperate" climate such as that of Boston, Mass.; a "cool" climate (Minneapolis or Denver); a "hot-humid" climate (New Orleans or Charleston, S.C.), and a "hot-arid" climate (Phoenix).

Dangerous Properties of Industrial Materials. N. Irving Sax. 1258 pages. Van Nostrand Reinhold (Litton Industries), 450 W. 33rd St., New York, N.Y. 10001. 1975. $42.50.

This book covers all areas of hazard, and provides information never heretofore presented. Among these is radiological pollution; complete Threshold Limit Values (TLV) with proposed changes; potential dangers of solid waste misuse; microwave, laser, and ultraviolet exposure from the control standpoint; and procedures involved in developing legislation for dangerous industrial material control. The author is the editor of *Industrial Pollution*.

Proceedings of the Second International Conference on Waste Oil Recovery and Reuse. 155 pages. Association of Petroleum Re-refiners, 1730 Pennsylvania Ave., N.W., Washington, D.C. 20006. 1975. $25.

Many benefits can accrue from waste oil recovery, re-refinement, and reuse. The Proceedings explain these benefits, give industry case histories, and discuss problems involved and suggested solutions. The world outlook for lubricating oil technology and conservation is discussed, as is the West German experience with oil reuse over six years. Sen. Pete V. Domenici (R-N.M.) keynotes the proceedings.

Harnessing the Sun to Heat Your House, 2nd ed. John Keyes. 208 pages. Morgan & Morgan, Inc., 145 Palisade St., Dobbs Ferry, N.Y. 10522. 1975. $2.95, paper.

This revised and expanded edition provides practical plans for a solar furnace compatible to most homes. The furnace is self-contained. Ways of storing solar heat are also given. The author estimates that the furnace could cut fuel bills by 30–90%. Technical data to back up the author's instructions and estimates are provided.

The Earth in the Looking Glass. Lloyd Darden. ix + 324 pages. Anchor Press/ Doubleday, 501 Franklin Avenue, Garden City, N.Y. 11530. 1974. $7.95, hard cover.

Selected by Publishers Weekly as one of "the best scientific/technical books of 1974," this book concerns the use of remote sensing by satellites to study the earth's total environment. Many aspects—agricultural and mineral resources, pollution in air, water, and wilderness areas, impact of science and technology on polar regions—and other pertinent topics are covered.

Environmental Impact of Stratospheric Flight. xiii + 348 pages. National Academy of Sciences, 2101 Constitution Ave., N.W., Washington, D.C. 20418. 1975. $8, paper.

What will happen if more supersonic and subsonic aircraft fly in the stratosphere? How and to what extent would stratospheric ozone be affected, and what would the ripple effects of increased ultraviolet radiation and other changes be? These questions are thoroughly examined, and approaches to solutions to these problems are presented.

The Water Resources and Development Market in Europe. 225 pages. Frost & Sullivan, Inc., 106 Fulton St., New York, N.Y. 10038. 1975. $595.

What will this market be for the next 25 years? This report makes a comprehensive forecast from the standpoints of the general problem, resource planning and development, technology, economic factors, markets, and the water supply industry. Countries covered are Belgium, France, Italy, the Netherlands, Luxembourg, Spain, Switzerland, the U.K., and West Germany.

First International Symposium on Ozone for Water & Wastewater Treatment. Rip G. Rice and Myron E. Browning, Eds. xxxviii + 910 pages. International Ozone Institute, 24 Central Ave., Waterbury, Conn. 06702. 1975. $45, hard cover; $40, paper.

This volume consists of the papers presented at the first symposium of its kind, held in December 1973. It covers ozone chemistry, monitoring/analysis, engineering aspects, generating equipment, and numerous pollution control applications.

Best's Safety Directory. 1000 pages. A. M. Best Co., Dept. P, Oldwick, N.J. 08858. 1975. $20.

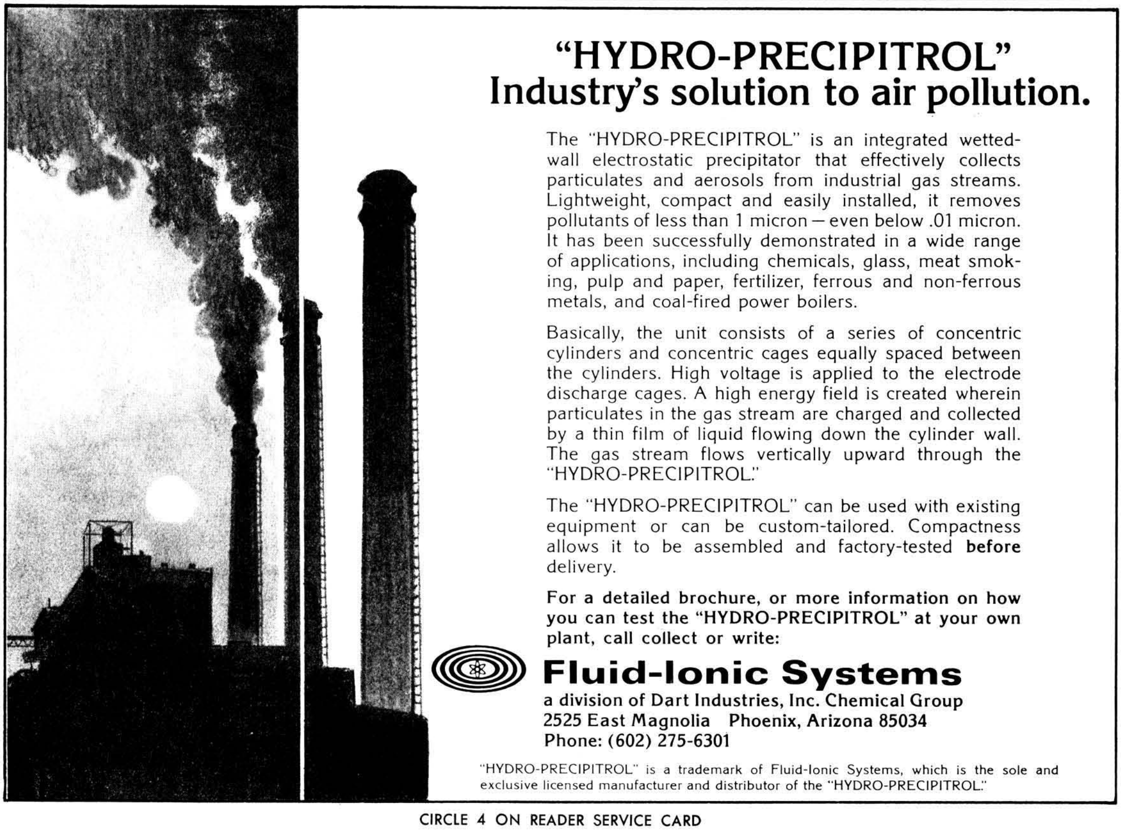
A complete source reference for plant safety, security, and industrial hygiene equipment and services. The book gives up-to-date industrial safety and security techniques, as well as the latest OSHA guidelines and standards, arranged according to the type of hazard. Over 3500 product classifications are contained in 12 major sections and 80 subsections.

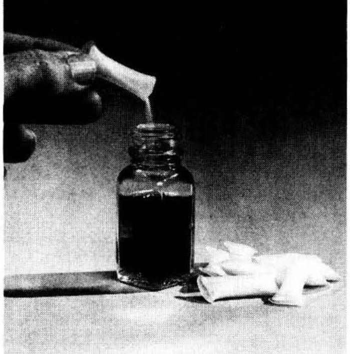
Environmental Dynamics of Pesticides. Rizwanul Haque and V. H. Freed, Eds. viii + 387 pages. Plenum Publishing Corp., 227 W. 17th St., New York, N.Y. 10011. 1975. $29.50, hard cover.

Pesticides have helped to increase world food production; yet they have entered the biosphere as persistent toxic chemicals. Once these pesticides have entered the biosphere, however, what is their fate? The authors present a very comprehensive treatment of this most important topic.

Toxicity of Vinyl Chloride—Polyvinyl Chloride. Irving J. Selikoff and E. Cuyler Hammond, Eds. 337 pages. The New York Academy of Sciences, P.O. Box 5075, F.D.R. Station, New York, N.Y. 10022, 1975. $35, paper (add 60¢ for mailing in the U.S., and 75¢ for mailing outside the U.S.).

Recent work done on vinyl and polyvinyl chloride was covered at a conference held in May 1974, of which this book is the outgrowth. It covers many clinical problems, and recognizes the carcinogenicity of the chemical. Pathology and epidemiology are discussed.





MEETING GUIDE

July 21–23 Gainesville, Fla.
Second Annual Conference on Research, Development and Design. Environmental Engineering Division of the American Society of Civil Engineers and the University of Florida

Program includes sessions on water quality modeling, sludge handling and leachate control. *Write:* P. L. Brezonik or J. P. Heaney, Dept. of Environmental Engineering Sciences, University of Florida, Gainesville, Fla. 32611

July 21–23 Portland, Ore.
Conference on the Magnitude and Deployment Schedules of Energy Resources.
The Energy Research and Development Administration, the Pacific Northwest Regional Commission and the Oregon State University Office of Energy Research and Development

Write: The Oregon State University Office of Energy Research and Development; 219 Covell Hall, Corvallis, Ore. 97331

July 21–24 San Francisco, Calif.
Fifth Intersociety Conference on Environmental Systems. The American Society of Mechanical Engineers (ASME), the American Institute of Chemical Engineers, the Aerospace Medical Association and others

Write: Paul Drummond, Director, Meetings, ASME, 345 E. 47th St., New York, N.Y. 10017

July 21–25 San Diego, Calif.
Second Annual International System Safety Conference. The National System Safety Society

Theme is "Survival in a Technical World." *Write:* J. Frederick Medford, c/o TRW Systems Group, One Space Park, Redondo Beach, Calif. 90278

August 3–8 Rindge, N.H.
Particulate Matter Systems. Engineering Foundation

Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 5–7 Boulder, Colo.
ASTM Symposium on Calibration—Problems and Techniques. ASTM Committee D-22 on Sampling and Analysis of Atmospheres

Emphasis will be placed on the calibration of analytical instruments used for the measurement of pollutants in ambient air, stationary sources and mobile sources. *Write:* ASTM, 1916 Race St., Philadelphia, Pa. 19103

August 8–10 Kansas City, Mo.
Annual Meeting. The American Academy of Clinical Toxicology

Write: Dr. Walter J. Decker, Lt. Col., MSC, U.S. Army Medical Laboratory, Fort Sam Houston, San Antonio, Tex. 78234

August 10–13 San Antonio, Tex.
30th Annual Meeting. Soil Conservation Society of America

Theme is "Land Use: Food and Living." *Write:* Soil Conservation Society of America, 7515 Northeast Ankeny Rd., Ankeny, Iowa 50021

August 10–15 Henniker, N.H.
Conference on Improving the Effectiveness and Efficiency of Scientific and Technical Information. Engineering Foundation

Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 10–15 Rindge, N.H.
Conference on Coal Preparation for Coal Conversion Processes. Engineering Foundation

Environmental impacts of coal preparation operations will be discussed. *Write:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 14–15 San Francisco, Calif.
Land Use and Environmental Regulations. Practising Law Institute

Write: Ms. Helen M. Davis, Practising Law Institute, 810 Seventh Ave., New York, N.Y. 10019

August 17–22 Rindge, N.H.
Mixing Research. Engineering Foundation

A session will be devoted to "Mixing in Waste Treatment Processes." *Write:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 17–23 Kingston, R.I.
3rd International Biodegradation Symposium. The Biodeterioration Society

Write: Dr. R. W. Traxler, Chairman, 231 Woodward Hall, University of Rhode Island, Kingston, R.I. 02881

August 18–20 Anaheim, Calif.
Second National Conference on Municipal Sludge Management and Disposal. Information Transfer, Inc.

Write: Harold Bernard, Program Coordinator or Debbie Littman, Conference Coordinator, Information Transfer, Inc., 6110 Executive Blvd., Suite 750, Rockville, Md. 20852

August 18–22 Newark, Del.
10th Intersociety Energy Conversion Engineering Conference. Institute of Electrical and Electronic Engineers, American Institute of Chemical Engineering, American Chemical Society and others

Topics will include solar buildings, nuclear power, geothermal power, fuel cells and others. *Write:* Mr. Daniel S. Goldin, General Chairman, IECEC, TRW Systems Group, M5/0259, One Space Park, Redondo Beach, Calif. 90278

August 18–22 New Hampton, N.H.
Environmental Sciences: Air. Gordon Research Conferences, Inc.

Write: Alexander M. Cruickshank, Director, Pastore Chemical Laboratory, University of Rhode Island, Kingston, R.I. 02881

August 24–29 Rindge, N.H.
Conference on Environmental Aspects of Hydroelectric and Pumped Storage Projects. Engineering Foundation

Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 25–27 Philadelphia, Pa.
Conference on Environmental Health Management. The International Safety Academy

Write: International Safety Academy, 1021 Georgia Ave., Macon, Ga. 31201

August 25–29 Syracuse, N.Y.
Conference on Metropolitan Environment: Vegetation, Spaces and Structures for Human Amenities. State University of New York (SUNY)

Write: Dr. Lee P. Herrington, SUNY College of Environmental Science and Forestry, Syracuse, N.Y. 13210

August 27–29 Philadelphia, Pa.
Environmental Aspects of Chemical Use in Printing Operations Conference. U.S. Environmental Protection Agency

Write: Franklin A. Ayer, Conference Coordinator, Research Triangle Institute, P.O. Box 12194, Research Triangle Park, N.C. 27709

Courses

July 21–23 Madison, Wis.
Environmental Noise Survey Techniques Workshop. University of Wisconsin—Extension

Fee: $295. *Write:* Donald E. Baxa, Dept. of Engineering, University of Wisconsin—Extension, 432 N. Lake St., Madison, Wis. 53706

July 21–25 Los Angeles, Calif.
Ocean Engineering: Energy Development and Environmental Control. University of Southern California, Continuing Engineering Education

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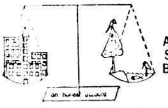

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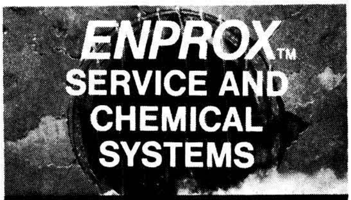

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143	144	145	146	147	148	149	150	151	152	153	154	155	156
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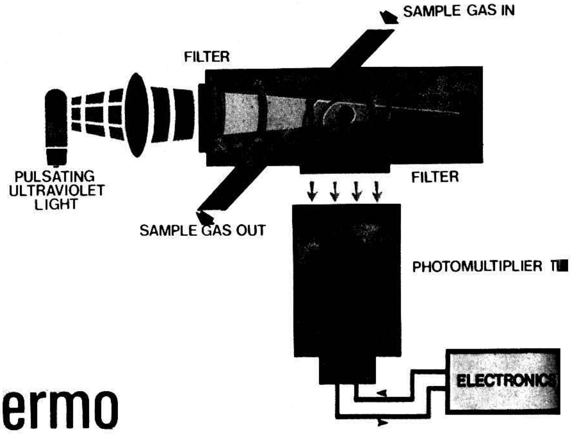
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