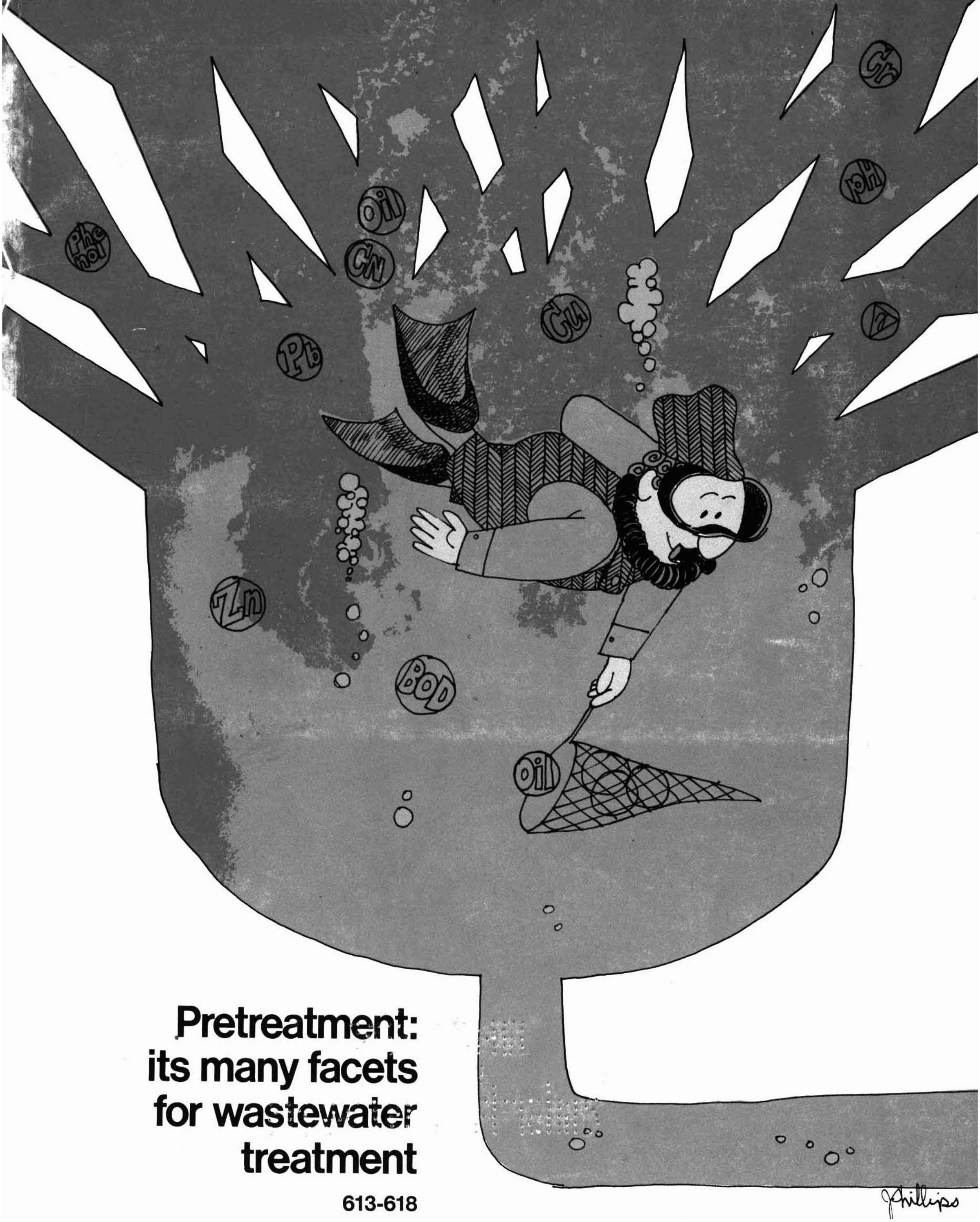
Environmental
Science & Technology

✓JULY 1974



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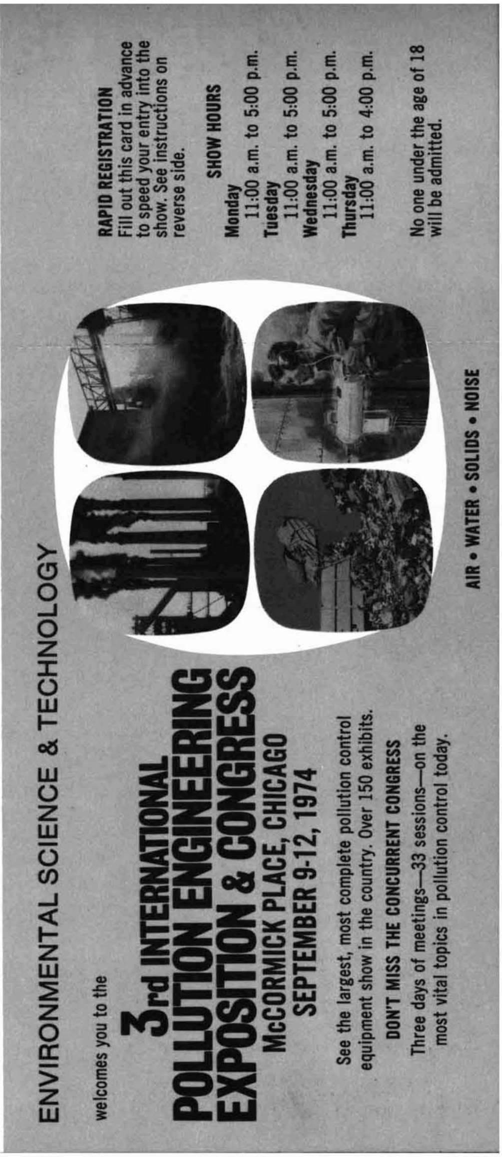

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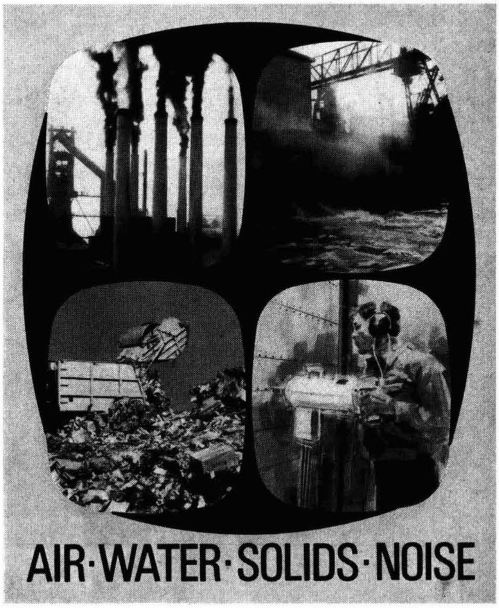
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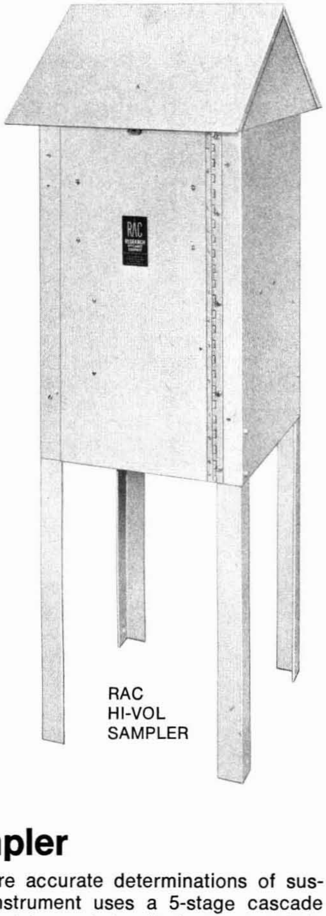

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Volume 8, Number 7, July 1974

ESTHAG 8 (7) 589-680 (1974)
ISSN 0013-936X

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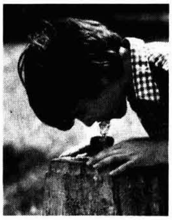

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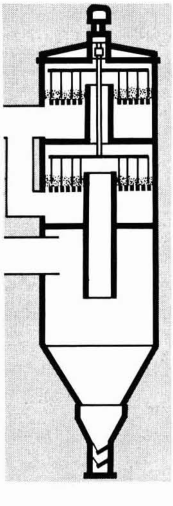

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Published monthly, with additional Pollution Control Directory in November, by the American Chemical Society, from 20th and Northampton Sts., Easton, Pa. 18042. Executive offices: Editorial Headquarters, 1155 16th St., N.W., Washington, D.C. 20036.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

ES&T ON MICROFILM: This publication is available on microfilm. For information, write to: Microfilm, Special Issues Sales, ACS, 1155 16th St., N.W. Washington, D.C. 20036.

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Published by the
AMERICAN CHEMICAL SOCIETY
1155 16th Street, N.W.
Washington, D.C. 20036

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For author's guide and editorial policy, see June 1974 issue, page 549, or write Katherine I. Biggs, Manuscript Reviewing Office, *ES&T*

Industrial steppingstones

Taking the first step in any endeavor is the hardest. It is also the most important as well as the most memorable. It has a lot to do with initiative, as anyone who has ever watched a baby take its first step will agree.

Similarly, some industries are taking their baby steps. For these it is the most important step ever. For all it's the step after which others can be taken. And so it goes with pretreatment, a first step that industries are taking on the long road to zero discharge of pollutants.

ES&T's Lena Gibney distinguishes compatible pollutants and finds that 31 industries are doing it. At the same time other industries are pretreating their waters, not for disposal but for in-plant use. Feature authors Luttinger and Hoché point out that reverse osmosis systems are right on for a number of industries who need ultrapure water. RO systems have already found use for process water for the electronics industry, boiler feed water for utilities, to mention a few.

Many will wonder why these pretreatment steps were not taken earlier. Some will simply point out that there was no requirement to do so; others rely on the economic argument. Pretreatment is a cost factor; it is nonproductive use of revenue.

By now, however, an environmental consciousness has surfaced. At times it may be difficult to perceive. Nevertheless, it is operative and will continue to strengthen, like an infant's self-assurance and reliance on walking.

What these industries are doing, or being required to do by the Federal Government under P.L. 92-500, is to limit their discharge of certain specified pollutants, those incompatible with the municipal treatment plant connected with that industry. By limiting such discharges, the municipal system is not thrown a curve ball.

As we move into fiscal year 1975, some industries will begin and others will continue to pretreat waste waters. Competitive systems will become more of a common practice before the dawning of the age of zero discharge of pollutants.

Stanton Miller

LETTERS

Reclamation

Dear Sir: The article on phosphatic clays (*ES&T,* April 1974, p 312) was a well-written and comprehensive survey of a very difficult environmental problem, although the title ("Those Nasty Phosphatic Clay Ponds"), in my opinion, did not reflect the tone of the article.

The article indicates that very little reclamation of slimes storage ponds is taking place, citing Bureau of Mines statistics that less than 1 mi^2 has been returned to productive use. In actual fact, over 6000 acres of old settling areas have been reclaimed or are in the process of being reclaimed. By reclaimed, I mean put to productive use. Typical uses include: improved pasture, truck farming, municipal parks, golf courses, campgrounds, and light industry.

The definition of reclamation as "generally meaning choked with wild plant growth and blending into local scenery," is not one that has been used by the industry. There are over 20,000 acres of old settling areas that meet such a description, and most of them appear to serve a useful function as thriving wildlife areas. Considering the present trends in the industry, combined with the pressures of a burgeoning population in central Florida, we can anticipate eventual reclamation of essentially all of these areas, probably within the next 10 to 20 years.

Leslie G. Bromwell
Florida Phosphatic Clays Research Project
Lakeland, Fla. 33802

Fabric filter correction

Dear Sir: *ES&T* published a list of air pollution control manufacturers with an indication of the various types of collectors which they had to offer (*ES&T,* April 1974, p 307).

American Air Filter Co. was inadvertently left out as a supplier of fabric collectors. We do, indeed, offer a wide variety of fabric collectors and would appreciate being listed as a supplier of this particular type of collection equipment the next time this list is published. The other listings for American Air Filter were correct.

Robert D. Moore
American Air Filter Co., Inc.
Louisville, Ky. 40201

DDT

Dear Sir: It is unfortunate that Robert Devlin ("DDT: A Renaissance?" *ES&T,* April 1974, p 322) did not have the benefit of the letter to the editor from Bert Van Tassell of Nutrilite Products, Inc., prior to writing his article. Devlin's statement that, "The only effective control of the tussock moth is DDT . . ." is apparently incorrect. Van Tassell reported that the two biological controls tested by Nutrilite Products, tussock moth virus and Bacillus thuringiensis, seemed to provide better results than DDT without affecting other life forms.

What concerns many environmentalists about DDT is its indiscriminate use when safer, biological controls exist. Granted, the use of DDT has had many beneficial effects, but its unlimited use when less damaging alternate methods exist, is like using a shotgun to kill a fly (or a tussock moth). A renaissance of DDT for uses where alternate, less harmful controls exist, would be most unfortunate and environmentally detrimental.

John Musgrove
Houston, Tex. 77034

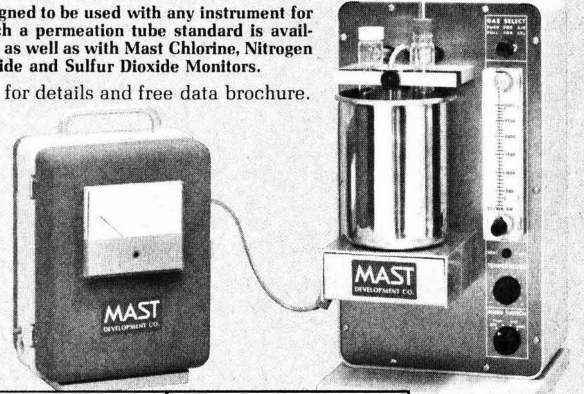
Solid waste as fuel

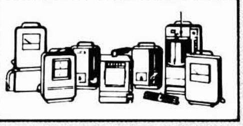
Dear Sir: The article "Liabilities into Assets" (*ES&T,* March 1974, p 210) seems unrealistically optimistic. It gives urban refuse generation as 136 million tons per year, with a heat content of 1433 trillion Btu. This supposedly could produce 136 billion kWh of electrical power.

The more recent studies indicate refuse generation is more like 115 million tons per year. We are aware of no data that would justify a near-term heating value projection greater than about 4500 Btu/lb. This would give a heat content projection of roughly 1000 trillion Btu.

Furthermore the conversion of heat to electrical power given implies that a Btu of energy in refuse is fully equivalent to a Btu in coal or oil. This is not true. If refuse is fired in a form relatively near its original state all or most of its energy will be delivered to the furnace, but a smaller fraction of its heating value will be available than for coal or oil. Compared to oil or coal, the penalty due to increased moisture in the flue gas will be 8–9% of the fuel's energy. The higher excess air required to burn refuse on grates will cost another 4% under the best of conditions. The excess air penalty for firing shredded refuse probably will be much smaller. However, shredding requires energy and the net result will be no better. Therefore the upper bound of the equivalent heat control must be reduced to less than 900 trillion Btu.

If more sophisticated waste derived fuels are considered, the energy loss penalty involved in combustion becomes smaller. However, the





processing stage required to produce the new fuel from the original refuse consumes more and more energy. As a result, the maximum net energy delivery approaches half of the original energy in the refuse.

We also would quarrel with some of the more specific conclusions later in the article. There seems to be no justification for the statement that CEA's Eco-Fuel "will generate as much steam as pulverized coal on an equivalent weight basis." The heating value given is 6900 Btu/lb which is considerably lower than coal's. Furthermore the combustion loss associated with the latent heat of water in the flue gas would be significantly higher. The operational excess air level is not given for the double vortex burner and therefore relative flue gas cannot be estimated.

Another point that should be taken more seriously is density. At 7–10 lb/ft^3, shredded refuse is not particularly storable or transportable. Its potential utilization thus is severely restricted.

We do believe in energy recovery from wastes. However, until projections and plans are put on a realistic basis—which considers the negative as well as the positive aspects—very little real progress is going to be made.

Alfred C. W. Eggen
Ronald Kraatz
K. T. Lear Associates, Inc.
Manchester, Conn. 06040

Waste oil recovery

Dear Sir: In general the subject matter of the meeting, The First International Conference on Waste Oil Recovery and Reuse (*ES&T*, April 1974, p 310–311), was covered quite well. However, the "specifications for re-refined oil" as set out in the block table are not technically correct, and, by implication, misrepresent the capabilities of re-refined oils and may be grossly misleading to readers not familiar with the detail of lubricant formulation.

The SA, SD, SE grades listed in the table refer to the API Service Classifications for automotive engine oils. Series 3 refers to a diesel engine oil specification developed by Caterpillar Tractor. Oils meeting these specifications must pass carefully defined engine tests and other laboratory tests. Meeting the requirements of these tests demands a careful formulation of base oil and additives. The properties listed in the table do not represent the specifications for the API Service Classifications, nor should the conclusions be drawn from them that used oils can be re-refined to meet any of these service requirements.

No test data were available at the conference to demonstrate that re-refined oils produced by current processing methods can be formulated to meet defined quality. This is a lack which needs to be filled. Unfortunately, the testing is relatively expensive. And even for products formulated with virgin base oils, a given specification is limited to base oil from one specific source (i.e., one refinery and one general type of crude oil). These limitations become prohibitive with respect to the variable input and relatively low volume output of a single re-refining plant.

It is likely that re-refined oils can be formulated with additives to achieve desired performance levels, but it should not be assumed that this can be accomplished by fiat merely by direct substitution of re-refined base oils for virgin base oils in a successful new oil formula. The proper and advantageous use of so-called "waste" oil is a worthy problem, but it is not a simple one.

S. M. Darling
The Standard Oil Co. (Ohio)
Cleveland, Ohio 44128

Solid waste information

Dear Sir: I should like to tell your readers about a service that I have recently utilized and found to be helpful in my environmental studies. This service is the Solid Waste Information Retrieval System (SWIRS) run by EPA's Office of Solid Waste Management Programs. The address for this service is: SWIRS, P.O. Box 2365, Rockville, Md. 20852. Recently, I sent a letter to SWIRS requesting information on participation of the public in solid waste management decisions and activities. I received a packet of materials in response which is apparently the usual response to inquiries. The information package included: a selection of abstracts of periodical and nonperiodical publications retrieved from the SWIRS data bank; xeroxed materials concerning relevant EPA grant and contract activities; and general reference materials. Each abstract had a complete bibliographic citation. In addition, I received, later, a number of books and pamphlets from the OSWMP publications office.

I found the information that I received from SWIRS to be very useful. The abstracts sent to me had obviously been selected according to their relevance to my own interests. In addition, the people at SWIRS are very prompt; I received a response to my inquiry within two weeks of the date that I mailed it.

Since receiving my materials, I have mentioned SWIRS to a number of my colleagues and have found that very few of them had heard of it. I am writing this letter in the hope that you will be able to help me inform your readers of this valuable service that they should often be able to find useful. The services of SWIRS are available free of charge. I believe that SWIRS is set up to handle inquiries which concern the economic and management aspects of solid waste handling, scientific and technical questions, and areas of public concern on environmental matters.

Jeannette McConnell
Glassboro, N.J. 08028

Mining industry

Dear Sir: The article on coal mine waste and acid mine drainage (*ES&T*, Feb 1974, p 110), left out some critical points. The most hazardous problem associated with coal waste has been its impoundment of water. In 1972, a coal refuse dam built by Pittson Co. in West Virginia to settle and filter wastewater from its coal-cleaning operation, burst, drowning 126 people.. These inherently unsafe impoundments are unneccessary, since alternate means of treating coal preparation wastewater are economically available. Another point concerning coal waste is that, due to the recent increased demand for coal, some companies have found it economical to recover coal from old refuse piles, while at the same time reclaiming the area.

Acid drainage from abandoned mines remains the biggest pollution problem of the coal industry. Mine seals are usually ineffective and sometimes hazardous. A possible answer to both the coal waste and acid drainage problems is to put coal waste underground. Coal waste can be returned to active mines either in empty shuttle cars, or piped in a slurry form or by compressed air. Coal waste slurry can be injected through boreholes into abandoned mines. Filling the underground void with waste can be expected to greatly reduce acid formation by cutting down the available air along with water infiltrating from roof fractures. The fact that research has never been done on the extent to which acid is controlled by this method, is very unfortunate. Mine backfilling with coal waste was practiced over 100 years ago in Pennsylvania, and is done in one Utah coal mine today, as well as practically all mines in West Germany and Holland.

Finally, our organization resents the implication of your article that strip mining is necessary, and that opposition is based on purely aesthetic values and irrational fears. We invite the author to visit a strip mined West Virginia hollow during a heavy rainstorm and observe for himself the landslides, increased flooding, and water pollution which are regular occurences in these areas. All of this destruction is unneccessary because over 95% of our recoverable coal can only be deep mined.

Ed Light
Campaign Clean Water
Charleston, W.V. 25322

CURRENTS

INTERNATIONAL

The United Nations Environment Program (UNEP) held a second session of its Governing Council in March in Nairobi, Kenya. The 58-member nations Governing Council agreed to fund UNEP at a level of $18 million in 1974 and $20 million in 1975 and assigned high priority to GEMS (the Global Environment Monitoring System), including more attention to the monitoring of radionuclides resulting from nuclear tests. NOAA administrator Robert White is spearheading the U.S. role in monitoring. Next session of the Governing Council is planned for April 1975 in Nairobi.

NOAA's Robert White

China has her pollution problems too, despite a law requiring that new industries be "clean" and existing industries clean up, according to a team of scientists from Penn State. On a 20-day tour in spring, they noticed that the bicycle-riding country is beset with dirty air from stacks and a shortage of energy. Trains are pulled by a steam locomotive burning coal, and there is no heat for homes or other institutions during the winter. Their water, however, is quite clean, having been treated with a flotation process to remove oil residues, followed by chemical treatment; the identity of the chemical was not revealed.

WASHINGTON

Commerce scientists link aerosols, global temperature. H. K. Weickmann and R. F. Pueschel of the NOAA (National Oceanographic and Atmospheric Administration) find that within 23 years the amount of manmade aerosol introduced into the atmosphere will equal the amount of natural aerosols. Natural aerosols stem from ash from volcanic eruptions, salt from the oceans, and dust blown up from the soil, whereas the man-made aerosols come from industrial sources and vehicles. The effect a given aerosol will have on climate depends in large part on how long it remains in the atmosphere. Some aerosols, such as lead from car exhaust, are rapidly removed by precipitation; others may remain in the stratosphere for months or years.

EPA is also concerned with aerosols. In a status report on sulfur oxides, EPA reports that recent reductions of sulfur dioxide emission in major cities have not controlled urban levels of acid sulfate aerosols.

EPA issued final regulations on unleaded gas availability. Beginning this month, some 111,000 gasoline stations are required to sell at least one grade of unleaded gas. The gas is required for 1975 model vehicles most of which will be equipped with catalytic converters. An estimated additional 10,000 gas stations in rural areas will be required to sell the unleaded gas beginning next year.

EPA administrator Russell Train suspended all pesticide aerosols containing vinyl chloride used in homes, food handling establishments, hospitals, or in other enclosed areas. Some 28 products were involved.

EPA's John Quarles endorsed a national mandatory deposit for beverage containers. In testimony on S. 2062, modeled after the beverage container law which was enacted by the State of Oregon in October 1972, the deputy administrator said, "We believe that a mandatory deposit program results in conservation of energy and materials and a reduction in solid waste and litter caused by beverage containers.

On the other hand, I. W. Abel, president of the United Steelworkers of America, testified that the proposed federal ban on nonreturnable beverage containers would result in 45,000–58,000 job losses in the metal and can industries, plus many thousands of jobs in related bottling industries.

The U.S. Supreme Court, in a recent decision, found that air pollution inspectors do not need a search warrant to enter a plant's unrestricted grounds to monitor smoke emitted from the plant stacks.

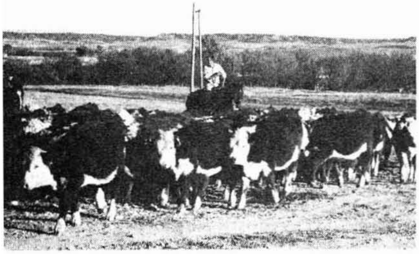
STATES

Wisconsin's city of Janesville has the answer to sewage sludge disposal. What began as a trial project by the University of Wisconsin (Madison) in an effort to comply with state orders to cut water pollution has proved effective. Sludge is applied to cropland as a low-grade fertilizer instead of the usual disposal methods of burning, burying, discharging into the nearest waters, or injection into the ground. Sludge-irrigated plots cropped with rye gave higher yields than plots irrigated with water. Corn and sorghum-sudan forage grasses planted after a rye harvest also showed better yields. Drawbacks, such as possible toxicity of heavy metals in the sludge to crops, are under study.

Residents in northeastern Alabama can look for better air as a result of the "scrubbing" undertaken by TVA (Tennessee Valley Authority) engineers at the coal-burning Widows Creek steam plant. The process will use a mixture of water and powdered limestone to solidify sulfur dioxide emissions which will then be washed away to a waste disposal area. At a cost of $42 million, the scrubber system will require 50 tons of powdered limestone per hour. Pumps with combined capacity of 150 mgd will be needed also to keep the water and limestone moving. An additional 75,000 tons of coal per year is necessary, however, to provide the heat and electricity for operation of the system.

Ohio's Erie Canal has received plutonium leakage from the AEC's (Atomic Energy Commission) weapons factory in Miamisburg. The radioactive plutonium, an isotope of the manmade poisonous metal plutonium-238, was found in the sediments under water. Since the metal was embedded deep in the mud and not found in the air or soil, AEC officials feel that there should be no health consequences to the population of some 897,000 (including the city of Dayton). Plutonium can cause instant death only if inhalated. There has been as yet no cause for the leakage, although the absence of the metal in air indicates that it had leaked out in a liquid effluent and not through a smokestack.

Some one-thousand Michigan cows were quarantined last month. Federal and state officials investigating a drop in milk production found that the feed contained contaminated magnesium oxide, a milk production booster. Brominated biphenyl, a fire-retardant chemical used in roofing and textiles, was accidentally blended with the magnesium oxide during preparation at Michigan Farm Bureau Services (Lansing) because of identical packaging. Some of the contaminated milk has already been distributed, but health officials feel that there is little health hazard to consumers since that milk was processed with milk from untainted cows during the packaging process.



Mich. quarantines cows

The Great Lakes gets another $3.5 million for pollution control from the EPA. The money will be used for joint U.S.-Canadian water quality studies under an agreement signed by the presidents of the two countries in 1972. Investigations will be twofold: water quality of the Lakes Superior and Huron; contributions of agricultural, forestry, and other land activities to water pollution and means of preventing future occurrences.

New York's first resource recovery plant will be built in Hempstead by the Hempstead Resource Recovery Corp. at a cost of $44.6 million. The facility will reduce residential and commercial wastes to less than 3% of original volume; generate 400,000 lb of steam per hour or enough electricity for the town residents and the Long Island Lighting Co.; recover 40,000 tons per year (tpy) of ferrous metals, 23,000 tpy of sorted glass, and 5000 tpy of aluminum. The installation will initially handle 2000 tons per day of raw, unsorted garbage after start-up in 1977, with expansion capabilities to 3000. Hempstead Corp. will operate the center for 20 years, sharing revenues with the town. Owens Illinois will buy the recovered glass, and U.S. Steel and Reynolds Metals the recovered metals.

MONITORING

Optical detection of aerosols has been made in the St. Louis region. Nephelometric sensing of the deliquescence of ammonium sulfate produced by reaction of sulfuric acid or ammonium bisulfate aerosol with ammonia provides a means of detecting these substances in air. Field experiments show them to be the dominant substances in the submicrometer, light-scattering aerosol in the St. Louis region, reports Robert Carlson of Washington University (St. Louis, Mo.).

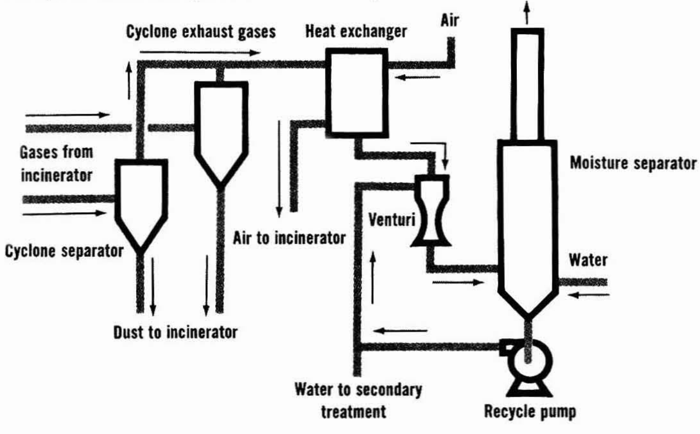
TECHNOLOGY

A "third generation" SO_2 abatement process known as "POWERCLAUS" uses a low-cost inorganic salt (sodium phosphate), eliminates the effluent associated with earlier techniques, and produces marketable elemental sulfur. Stauffer Chemical Co. (Westport, Conn.) has licensed Chemical Construction Corp. (New York City) to market the process. On a demonstration scale at Stauffer's carbon disulfide facility (Delaware City, Del.), and at Connecticut Light and Power Co. (Norwalk, Conn.), sulfur removal efficiencies were about 95% during the test period, with an on-stream factor of 99.8%. The next step would be a 50,000–100,000-cfm treatment facility.

Peat moss bed filtration removes heavy metals from wastewaters, according to a patented adsorption process. All heavy metals are brought to within EPA requirements. Coloring matter is also removed, as is oil up to 2% by weight concentration, and BOD is reduced by 80–90% (more with aeration). Cost is cut by 80%. One 16 × 8 × 9-ft module can handle 80,000 gpd, amd modules can be stacked or arranged side-by-side. Metal recovery may be feasible for larger electroplating or metal finishing shops. Couplan, Inc. (Sherbrooke, Que., Canada), has licensed Hussong-Walker-Davis Co. (Cornwall Heights, Pa.) to market the system in the U.S.

Removal of sodium bicarbonate and sodium sulfate particulate matter is effected at the American Oil Co. (AMOCO) refinery at Whiting, Ind., by two cyclones and a venturi scrubber system. The cyclones each handle 44,750 scfm at 1350°F. Inlet gas loading is 30 lb/min of particulate

CEA cyclone & scrubber system at AMOCO refinery



matter. The venturi system cools the gas stream to 180°F and removes particulate matter; a cyclonic moisture separator, which removes entrained exhaust droplets from venturi exhaust from a 316-tpd fluid-bed incinerator burning oily sludges and spent caustics, was supplied by Combustion Equipment Associates, Inc.

Over 90% SO_2 removal is achieved with a double-alkali scrubber which General Motors Corp. (GM) recently put into operation at its Chevrolet Motor Division plant (Parma, Ohio). The SO_2 from power plant flue gas is converted to an inert solid material suitable for landfills. The new system's problem is that it adds $10/ton to the cost of coal, including facility write-off. EPA has let a 1-yr contract to GM to study the design and construction "with an eye toward reducing both initial costs and operating expense."

Recovery of elemental sulfur from stack gas cleaning may be possible by treatment of Claus unit tail gas in the liquid phase, a process being checked by the Institut Francais du Petrole (IFP, Reuil-Malmaison, France). In the IFP SO_2 treatment method the reaction liquor is a polyethylene glycol with a proprietary catalyst in solution. The catalyst combines with hydrogen sulfide (H_2S) and SO_2 to form a complex. The complex reacts with more H_2S and SO_2 to regenerate the catalyst and from elemental sulfur of very good purity.

A process of separating thermoplastic film from otherwise recyclable waste paper was recently patented by James Laundrie of the U.S. Forest Products Laboratory, Department of Agriculture (Madison, Wis.). The plastic films, suspended with paper in air at 250–350°F, contract upon themselves and decrease their surface area in relation to their weight. Separation of paper and plastic by standard air classification techniques then becomes possible. This thermal separation process uses no water.

Old asphalt concrete can be recycled and made into a product virtually indistinguishable from asphalt concrete made from newly refined asphalt. This is accomplished by the RMI roadrunner which was developed by the Las Vegas Paving Co. (Las Vegas, Nev.). The roadrunner recycles old asphalt into hot mix with an additive, or processes newly refined asphalt, but allows no gaseous hydrocarbons to escape unburned. Savings on fuel and raw materials are achievable, and removal of an eyesore, in the form of waste asphalt piles, is possible. The system was described by Robert Dunning, owner of Petroleum Sciences/PAX International (Anaheim, Calif.).

INDUSTRY

Universal Oil Products Co. (UOP) dedicated its new automotive catalyst plant at Port of Catoosa, Okla., in May. UOP's Automotive Products Div. is processing monolithic catalysts at the new 134,600-sq ft facility to meet Chrysler Corp.'s requirements for cars and light-duty trucks for the next five years. John Logan, UOP's president and chairman, said that UOP has been developing processes to make more and better gasoline from crude oil for 60 years. He also said that UOP researchers have been investigating catalytic converters for the past 15 years as a method of cleaning up automotive exhaust emissions.

UOP's John Logan

Research-Cottrell chief executive John Schork announced that the company sustained a loss of $0.73/share ($3,071,000) in the second quarter ending April 30, 1974, as compared to a profit of $0.27/share ($1,103,000) in the corresponding period of 1973. The six months ending April 30, 1974, showed a loss of $0.49/share ($2,057,000) against a profit of $0.50/share ($2,077,000) for the previous year's corresponding period, despite an increase in sales from $60,650,000 to $66,406,000 over those periods. These losses were ascribed to problems with R-C electrostatic precipitator business in the U.S. and Canada, as well as material cost increases, shortages, and higher interest expenses. However, Schork foresees far more favorable results for the second half of 1974.

The Manufacturing Chemists Association (MCA, Washington, D.C.) has recently published a chronology concerning attention to occupational health aspects of vinyl chloride monomer (VCM). According to MCA, VCM's principal risks were first believed to be only those of fire and explosion, and that maximum safe concentration, above which anesthetic effects were noted, was deemed to be 500 ppm (1954; confirmed in 1962; OSHA standard 1971). This standard was later cut to 50 ppm (OSHA ruling, emergency basis, April), and after an MCA-administered study completed this May, a "no-detectable" standard was proposed by the Occupational Safety and Health Administration (OSHA) (*ES&T,* April 1974, p 301).

The Industrial Chemicals Division of Allied Chemical Corp. says that about 200 municipal wastewater treatment plants are using inorganic chemicals to precipitate phosphorus (P) and to reduce suspended solids (SS) by coagulation. Of these plants, over 100 are using alum, according to Allied. To answer questions about P, SS, and BOD problems and their chemical treatment, Allied has made available a special report, "Choosing the correct precipitant/coagulant." The report discusses precipitation and coagulation chemicals and other technical data to help select the proper materials for a given treatment plant (*ES&T,* May 1974, p 420).

The Boating Industry Associations (BIA, Chicago) completed a 2½-year, $750,000 study, one-third funded by EPA, which concluded that outboard motors do not affect water or its life systems harmfully. Matt Kaufman, project director, said that there were no acute or chronic effects, and that growth and reproduction of representative plants and animals in test lakes in Michigan and Florida remained virtually constant with or without outboard motors. Leaded and unleaded fuels were used; engines in Michigan were of the newer drainless type, but one Florida lake was tested with the older-type motor, from which unburned fuel may be drained. Fish taste and chemical content of water and bottom seemed unaffected.

Gravel bed filters clean industries' hot and abrasive dusts

Rexnord units clean air emissions on lime kilns in Arizona, clinker coolers in Florida, and a cement plant in Texas and is applicable for any dusts that tend to agglomerate

Despite the fact that there are only a few examples where the gravel bed filter has been applied and fully evaluated on an industrial scale, nevertheless there are 16 installations in the cement industry that will be using this device to clean up their industrial emissions by 1975. By the end of 1973, Rexnord had installed 116 units at 12 sites and will be installing another 127 units at another 11 sites. Hot and abrasive dusts from clinker cooler operations are one of the most difficult jobs for the gas cleaning equipment manufacturers, one reason being that the quickly changing gas temperatures and gas volumes make it difficult to control operations.

Rexnord Air Pollution Control Division (Louisville, Ky.) nevertheless, has eight units operating today. The first REX gravel bed filter on the North American Continent went into operation in July 1972. The unit cleans the gases from a lime kiln of the Kennedy Van Saun preheater type, at the Paul Lime Co. (Douglas, Ariz.)

Stack emission tests were conducted by the Engineering Testing Laboratories, Inc. (Phoenix, Ariz.) in July, September, and October of 1972. Actual stack particulate emissions were about one half of those allowed by the stringent process weight requirements in the state of Arizona. The performance was accomplished in spite of the actual gas volume being approximately 50% greater than what was originally designed for. The company then ordered a second unit which has been operating since July 1973.

For hot and abrasive dust control problems, these gravel bed filters achieve high efficiency, low operating costs, and no maintenance. They operate at high temperatures (up to 900°F) with minimum maintenance, no bags, no water, and no replacement filters. The filter medium itself is relatively unaffected by temperatures up to 2000°F. In general, the unit can be applied to any dust which agglomerates. And although they have been used or ordered for dust separation in cement plants and lime industries, they may soon be finding application in other industries.

Other installations

The control of abrasive dusts has been confirmed in another geographic location. For example, General Portland, Inc. installed three units on three clinker coolers at their Tampa, Fla., plant between June and August 1973. Their spokesman reaffirmed earlier experience. Plant manager Bob Johnson says, "Applicable Florida standards were achieved."

General Portland's Johnson
Meeting Florida standards

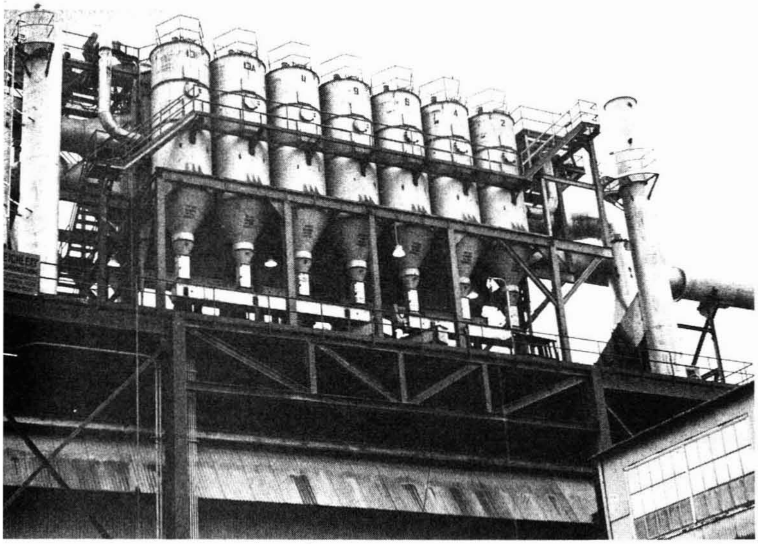
Then in August 1973, the units were installed by the Universal Atlas Cement Division of U.S. Steel in their operation at Waco, Tex. Plant manager Tom Ryan reports that compliance testing was performed by Ecology Audits (Dallas, Tex.) and are in compliance with Texas air pollution standards.

Despite the fact that these units are being used extensively by the cement industry in the U.S., other studies are indicating the usefulness of these units to control emissions from sinter plants in the steel industry, glass furnaces, fly ash, as well as other applications where hot and abrasive gases have to be cleaned.

At the installations tested, effluent quality has been well within the new source performance standard for portland cement operations (ES&T, Oct. 1972, p 886).

The European connection

As you may be aware, the gravel bed filter on the North American Continent is built in accordance with an exclusive licensee agreement between Gesellschaft für Entstaubungsanlagen (GfE) (Munich, Ger.) and Rexnord, Inc. (Milwaukee, Wis.). Prior to this agreement of March 8, 1972, the German company, GfE had built more than 150 gravel bed filters inside and outside Europe. The largest number of these were installed to clean gases from cement clinker coolers, one of the hottest and most abrasive dusts needing controls. Based on European experience, the unit is capable of achieving high efficiency and for all intents and purposes requires no maintenance, even when the most difficult clinker cooler application is considered.



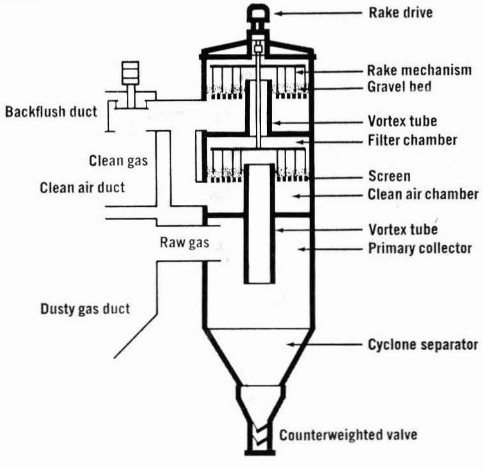
Controls. *Emissions are well within EPA new source performance standards for portland cement plants*

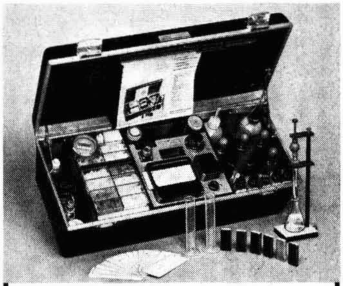
Why gravel beds?

Chief attributes of these units include:

- High performance is achieved without any necessity for maintenance
- Unit accommodates quickly changing gas temperatures and volumes and handles abrasive dusts. This combination is one of the most difficult applications of gas-cleaning equipment
- Applicable standards are met at the lowest possible operating costs
- A wear-resisting filter medium which will withstand much higher temperatures than fabric filters
- Low maintenance costs because of minimal moving parts and no necessity to replace the filter medium
- Temporary surges of gas volume, dust loading, or gas temperatures, such as from normal 500–900°F maximum, will not seriously affect equipment or performance
- Relatively wide variations in dust particle size will not significantly affect filter performance
- No dilution air required for very high temperatures. Almost complete independence from the dust particle structure
- Occasional red-hot sparks will not damage the filter medium

How it works





INTERNATIONAL

European water cleanup is under way

Common market countries and others are taking measures to curb discharge of industrial effluents to waterways

The plethora of emerging laws, both at the national and international levels, that deal with control of water pollution came into sharp focus in Amsterdam, Holland, in May. There, some 200 delegates from 17 countries participated in a three-day conference titled, "Industrial Waste Water and Disposal Within the European Economic Community," organized by the U.K.'s Society of Chemical Industry and its Industrial Water and Effluents group.

Although, as the conference title suggests, discussions centered mainly on the nine-member EEC countries—Belgium, Denmark, France, West Germany, Ireland, Italy, Luxembourg, The Netherlands, and the U.K.—the fact that attendees came from the U.S., Canada, Australia, and elsewhere served to point up the common concern shared by all over pollution of water and the desire to share experiences, technical expertise, and to learn from experiences of others.

The Rhine, a special case

In her opening address, Irene Vorrink, Holland's Minister of Public Health and Environmental Hygiene, made the impassioned plea, "Do not require mothers to keep their children from water, not because it might drown them but because it might poison them." It was natural, too, that Mrs. Vorrink should make special reference to the pollution of the Rhine, one of Western Europe's major rivers which has of late acquired the dubious distinction of being classed as Europe's longest sewer, for Holland is on the receiving end of pollutants that pour into the Rhine as it passes from Switzerland through West Germany and France before traversing Holland on its way to the sea.

At the December Ministerial Conference on Rhine Pollution in Bonn, Mrs. Vorrink pointed out that agreement was reached on establishing three categories of discharge relating to their degree of offensiveness. Substances on the "Black List"—compounds of mercury and cadmium, pesticides based on organophosphorus, and the like—should be prohibited from entering the river.

There should be limited discharge of "Gray List" materials—mineral oils, cyanides, fluorides and metals such as zinc, copper, and lead, and substances that give rise to bad taste and odors. "Beige List" items, those that adversely influence the oxygen content or damage the water, should be subject to discharge regulations still to be decided. Mrs. Vorrink said, "It will be necessary to put increasing emphasis on pollution abatement at the source. In my opinion, it is the task of the public authorities, as well as of industry itself, to stimulate development of clean technology."

International consultations about the Rhine aren't the only ones in the area of water pollution in the Europe-wide context. In April, an agreement became effective curbing pollution of the North Sea and parts of the North Atlantic and Arctic Oceans. Known as The Oslo Agreement, the 13 countries party to the pact—Belgium, Denmark, Finland, France, West Germany, Iceland, Ireland, The Netherlands, Norway, Portugal, Spain, Sweden, and the U.K.—put their signatures to the proposals in Oslo, Norway, in February 1972. It centers on both airborne and waterborne pollution.

A sequel to The Oslo Agreement was signed in Paris last September which relates to ocean discharges from rivers, estuaries, and pipelines. Earlier this year, the seven countries bordering the Baltic—Denmark, Finland, East and West Germany, Poland, Sweden, and The Soviet Union—agreed to restrictions to avoid polluting it.

Estuaries, also a concern

Pollution of estuaries and tidal reaches of rivers is one of the most severe problems, Denis Howell, U.K. Minister of State at the Department of the Environment, told attendees in his keynote address. "It was thought that the dilution available in such large bodies of water would be enormous. Consequently, we were relatively slow to introduce controls over large volumes of untreated or partially treated sewage and industrial effluents discharged into estuaries."

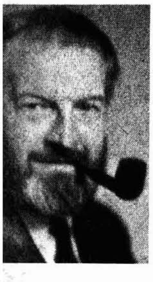
In fact, Howell points out, "In many cases the water in estuaries is only slowly replaced by fresh water or water from the sea, so that polluting discharges may stay in the vicinity for weeks." Moreover, he adds, "Estuaries are often much deeper than rivers so the ratio of surface area to volume and therefore the rate of oxygen supply is low."

For this reason, European countries are becoming increasingly concerned about pollution of estuaries and indeed beyond, to the sea. "We in the U.K. propose to control all discharges to the sea and we have supported work leading to the Oslo and Paris conventions," Mr. Howell says.

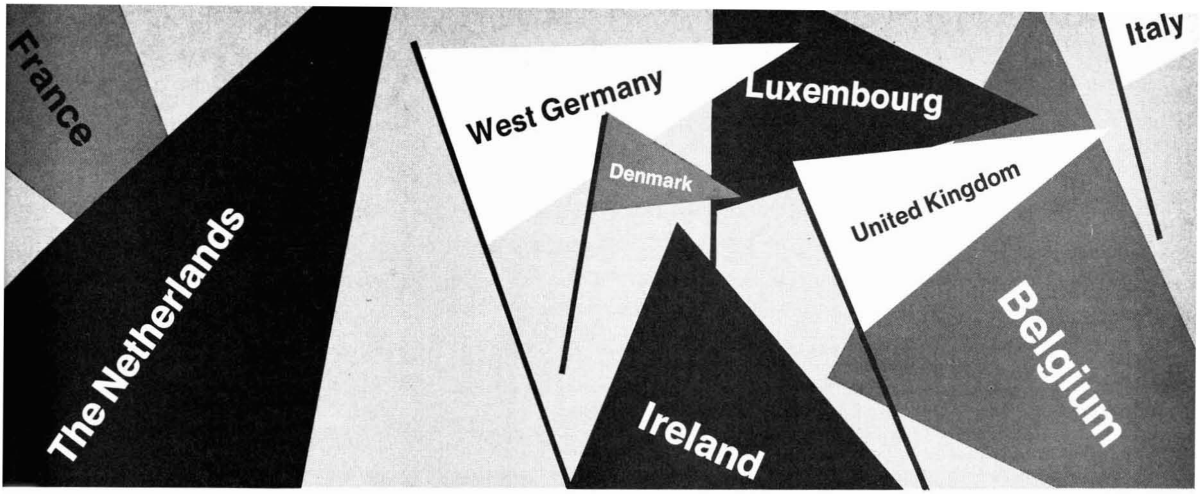
Amsterdam conference


Vorrink


Howell



This story was written for ES&T *by* **Dermot O'Sullivan,** *London bureau head for the ACS publication,* Chemical & Engineering News, *who attended the Amsterdam Water Conference in May.*



As evidence of this concern, a detailed study of the Tees Estuary on England's West Coast is now getting under way. The region is densely populated and the water pollution problem is exacerbated by the high concentration of industries in the area. Imperial Chemical Industries' huge petrochemical plants are on both sides of the river, at Wilton and at Billingham. In addition, there are oil refineries, steel mills, a fertilizer plant, and a host of heavy chemical operations there.

speakers air progress


Challis Scheltinga Salzwedel Johnson

Playing a key role in the Tees study is Edward J. Challis of ICI's Petrochemicals Division, Wilton, and chairman of his company's environment committee dealing with problems arising at ICI's operations throughout the U.K. and Western Europe. His philosophy is that the best solution to a pollution problem comes from an examination of the total system, the intake water, the effluent, and the purifying power of the receiving waters which, he maintains, experts often forget to consider.

"Pollution is simply the overloading of this natural purification power," he told the conference. "The objective should be to reduce the level of polluting matter to the point where the natural purification powers of the receiving waters can cope with it."

In the Tees Estuary Systems Study being led by the River Authority and in which Mr. Challis and his company are cooperating, the aim is to seek cheaper ways for the communities to clean their sewage and cheaper and more effective methods for companies to make a phased reduction of their pollution discharges. Toward this end, he and his associates are working closely with the local and national water authorities.

"Such cooperation is sometimes viewed as a cozy relationship," Challis admits. "But it isn't. It means establishing a mutual trust between industry and the regulation officials who are the policemen." An advantage he cites arising from such collaboration is that planned adjustments to industrial operations can be more effectively executed by the chemical engineers than when situations of sudden panic arise.

Laws already in effect

The U.K. takes pride in being one of the first countries anywhere to establish laws governing water pollution. These laws date back to serious outbreaks of cholera in London in the last century which led to a Public Health Act of 1848 and paved the way for sewer construction. A Gas Works Clauses Act in 1847 made it an offense to discharge wastes from gas works into streams.

And a Salmon Fisheries Act of 1861 made it an offense, "To cause or knowingly permit any liquid or solid matter to go into a stream so as to cause the fish to be poisoned." A few years later, the River Pollution Act of 1876 was passed. This, Denis Howell claims, was the first General Act for dealing with river pollution as an evil in itself and not as related to particular interests such as salmon fisheries.

Moving to more modern times, in 1945 the U.K. set up river boards to exercise pollution control functions. Since then, a system of consent controls was introduced for discharges of trade or sewage effluent into streams, and a Clean Rivers Act extended to estuaries and tidal waters. This year, the U.K. has reorganized the bodies responsible for water pollution control into 10 regional water authorities, each of which oversees two or more river basins in England and Wales. And a bill now before Parliament is aimed at giving these water authorities comprehensive control over all discharges whether to rivers, to sewers, or to the sea.

In the U.K., discharges of trade or sewage effluent into inland or coastal waters, including pipeline discharges into the sea, require the consent of a water authority. It is an offense to make a discharge without consent. But as Mr. Howell observes, "The concept of making the polluter pay for clearing up the pollution he creates is open to undesirable misinterpretation. We do not want to create a system where the polluter may continue to pollute so long as he pays for it. The only acceptable system of charging for discharges is one which is designed to achieve environmental objectives."

Polluter pays here too

The polluter-pays-principle is also the cornerstone of the Water Quality Act which The Netherlands passed in 1970. As in the U.K. and elsewhere, discharges of pollutants or harmful substances into surface waters is prohibited without government consent. Quality control of Holland's large rivers, estuaries, and territorial waters comes under the jurisdiction of the central government; that of the smaller rivers and watercourses is the responsibility of local county government.

The Act, notes Dr. H. M. J. Scheltinga who, in addition to being public health inspector at Holland's Ministry of Health and Environmental Hygiene in Arnhem, is a member of the U.S. Water Pollution Control Federation, "provides the tools to tackle and complete the cleanup of water pollution in the country. It seems likely that the official national aim, 'Control over water pollution by 1985,' will be reached, at least in respect to oxygen balance."

The basis of charging for both community and industrial discharges is the population equivalent (p.e.) oxygen demand. This is a measure of the average daily discharge of oxygen-demand substances per head of population. One p.e. unit represents 180 grams of oxygen demand per liter of water, calculated by a combined COD and NOD analysis.

The tax or charge per p.e. of pollution discharge varies according to the area of the country, the total load burden of the receiving water, and whether the discharge enters large rivers or smaller local ones. In general, the charge varies from a low of about $2.00 per p.e. to about $7.00. Next year, the government intends to broaden the scheme and introduce taxation of toxic wastes as well as oxygen-demand matter.

Dr. Scheltinga scotches the idea that a company might elect to pay a discharge tax instead of investing in systems for cleaning up their wastes or otherwise avoiding the pollution. "The authorities always have the option of refusing or withdrawing a discharge consent, even when a company is willing to pay, in cases where the water quality is very poor," he notes.

Water quality is a particularly critical one for Holland being, as Dr. Scheltinga puts it, "The basement of Europe." The three major rivers flowing through the country—The Rhine, The Meuse, and The Schelde—are international waterways. Moreover, Holland has one of the highest population densities anywhere. Averaging 1000 people per sq mi. In the heavily industrialized western part of the country, the figure is nearer to 5000 per sq. mi. Too, Holland has undergone a very rapid industrial growth since World War II. Two of the world's largest oil refineries are located at Rotterdam which is also among the world's busiest ports.

Laws in other countries

Speakers at Amsterdam also reviewed the water pollution measures being taken in France and West Germany. In France, the administration of the quality of inland waterways is shared by six regional basin authorities. Each oversees the behavior of water users both from the point of view of water abstraction and effluents discharged. They also subsidize the cost of building water treatment facilities. For industries, grants of up to 50% of the total costs are made. But infringement of discharge regulations can carry fines of up to $20,000 and possible jail sentences of six months.

In West Germany, the Federal Water Act of 1960 is a framework law within which each of the country's 11 states have their own individual water acts. A new federal law now being debated might follow the French system of subsidizing the building of water purification plants from taxes levied on polluters, although Prof. J. Salzwedel of the Institute for Studies on Water Resources Law at the University of Bonn, holds that "This regulation is a violation of the principle that the producer of the waste water has to pay. In the Federal Republic of Germany, there is more to be done regarding legislation if water pollution is to be reduced."

Right now, the greatest hope for coordinating the water quality plans for most of Western Europe rests with the Commission of the European Communities in Brussels which has drawn up an environment action plan for the nine member countries. There are numerous aims to the plan ranging from "preventing, reducing, and, as far as possible, doing away with the harmful effects of pollution and nuisances in the environment" to "seeking common solutions to environmental problems with states outside the community."

At the community level there is a drive toward standardization of sampling and measuring methods, harmonizing pollutant specifications, and preparing lists of quality objectives. However, Stanley P. Johnson of the Environment and Protection Service of the Commission believes that there tends to be too much stress on the adverse health aspects of pollution problems and not enough on the esthetics of the environment as a whole. "There may be other parameters that are more objectional than just the *E. coli* content of the water," he remarks.

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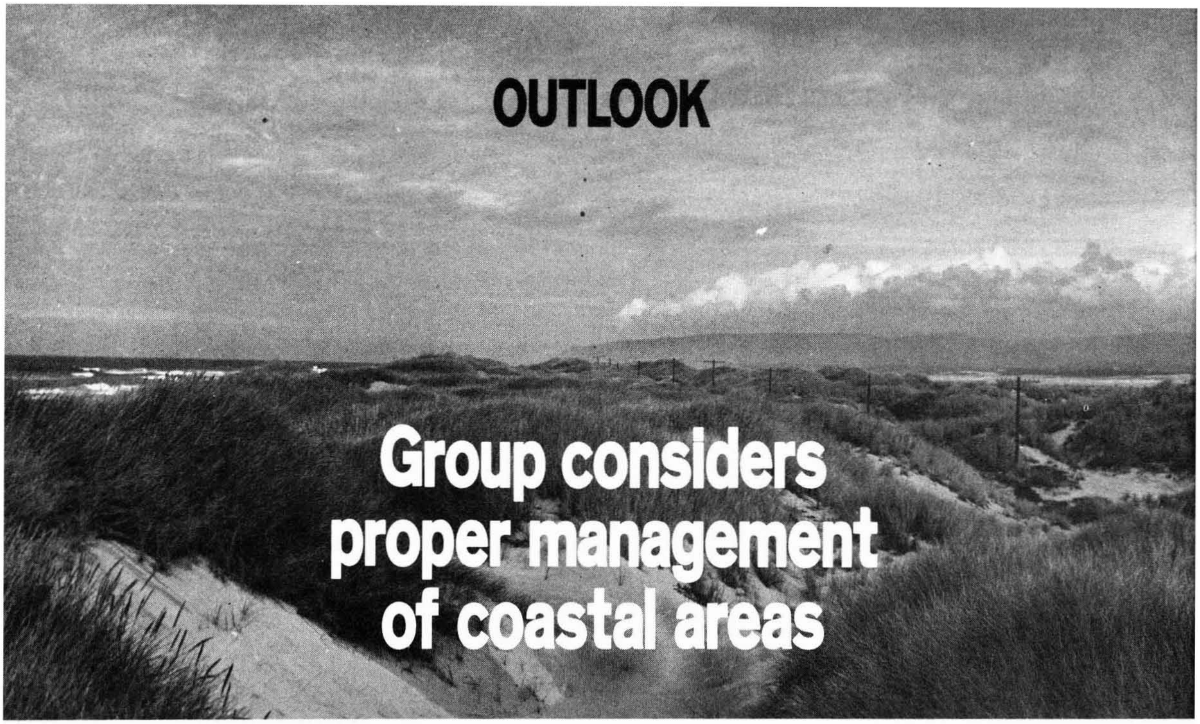


Group considers proper management of coastal areas

Conference hears need for balancing development and environmental considerations

Faced with massive increases in coastal zone development—both onshore and offshore—the U.S. is in a position to lose as much as it could gain, according to opinion voiced at the National Oceanic and Atmospheric Administration-sponsored Conference on Coastal Zone Management held recently in Charleston, S.C.

Speakers held that money may be good, but so are some of the less tangible qualities of coastal areas. And in order to assure a balance between the two a national coastal zone management program is needed, those attending the conference were told.

In keynoting the meeting, Sen. Ernest F. Hollings (D-S.C.), who long has fought for federal coastal zone legislation, pointed out that landfills during a 200-year period helped to create much of the port city of Charleston, but that this development also introduced some attendant ugly problems. For example, the Ashley River at Charleston has become polluted. The Cooper River there has become silted because of a hydroelectric project upstream, and ocean-going vessels have difficulty docking. Urban sprawl has "marooned" the older section of Charleston, and now there is no room for a causeway, except through a marsh, to free the flow of traffic. The paradox is that more development is needed to correct problems brought on by earlier development.

Sen. Hollings, however, says the problems are not insurmountable. Environmentally unique areas exist—both in terms of natural beauty and wildlife preservation—where development should not take place. But in areas where development has taken place, much can be done to reclaim what once was lost. He points out that the city of Charleston has built an excellent sewage treatment plant, and that oyster beds that were closed 47 years ago because of pollution were reopened last year. The value of the beds is estimated at $60 million, the Senator said.

Department of Commerce Secretary Frederick B. Dent took the occasion to announce the first-ever grants to help states set up coastal zone programs. The funds, which totaled almost $635,000 were awarded to Maine, Oregon, and Rhode Island by NOAA under the Coastal Zone Management Act of 1972. The money is "to encourage effective management, beneficial use, protection, and development along the nation's sea coast and Great Lakes shores." It is a matching-fund program whereby the states put up one third of the money.

Dent says the administration now is committed to the program despite the fact the federal office of Management and Budget (OMB) refused to fund it for its first year of existence. Dent pointed out an appropriation of $12 million is available this fiscal year (FY 1975) for the grants program, and that an additional $12 million for the program is being sought by the President as part of his present budget requests.

Development to increase

The Commerce Secretary also considered the problem of energy development, brought on by the recent crisis, the question of deep water ports, and the problems of extracting minerals from submerged offshore lands. What emerged was the administration's intent to go full-speed ahead in all three areas. Dent, however, says the environment, too, must be considered. As he put it, "Only through effective management of these valuable resources and the environment that supports them, can we hope to realize their full potential both as a provider of food as well as jobs."

Although many feel more authority is needed at the federal level if the problems of the nation's coastal zones are to be adequately handled, the thrust of the 1972 Act is toward setting up programs in each of the individual states. A paper prepared for the conference by Washington, D.C., consultant Harold F. Wise et al., stressed that the Coastal Zone Management Program "is primarily a state program." The paper pointed out that funds are provided to coastal states so they can identify their own interests and develop their own management mechanisms to protect those interests at the same time.

But the state must meld together a variety of private and public interests, which include the interest of the Federal Government. Thus, federal input in coastal zone programs is an assured thing. This input could come from such sources as the federal Energy Office; the Department of Defense, because of military establishments in coastal areas; the Environmental Protection Agency, which is responsible for air and water quality standards enforcement; the Corps of Engineers, responsible for permits for solid waste disposal in coastal waters and rivers; the Department of Commerce and its Office of Coastal Environment; and others. Generally, most states wanted a strong hand in meeting their coastal zone problems.

Sen. Ted Stevens (R-Alaska) is adamant in his desire for strong state support. He said, "We are trying through our state officials to identify Alaska's problems and to convince our federal agencies that, having identified these problems, we know best how to solve them." He noted particularly that rules and regulations that apply to the other 49 states are not relevant to nontemperate zones.

Sen. Stevens pointed to the necessity to consider Alaska as a unique situation rather than as part of a general U.S. program. In Alaska's coastal zone, there is every type of resource available anywhere in the other 49 states, and in greater abundance, he said. "Whether you are discussing timber or watershed management, oil and gas development, fisheries protection and management, mineral exploration or extraction, tourism, the recreational potential, agricultural or industrial development, or the needs and desires of a sprawling urban community, you cannot address problems of coastal zone management without involving Alaska's unique situation."

The local view

The local view of the national interest in coastal zone planning and management was discussed by Lee Koppleman, executive director of the Nassau-Suffolk (New York) Regional Planning Board. He outlined the areas in which the various levels of government could best contribute.

Koppleman said the identification of the most important coastal zone problems is well within local capability at the county, or even lower, level. However, he said, "Identification, assembly, and interpretation of natural science are clearly beyond local capability and probably beyond state capability, and should be a federal responsibility."

Application of local economic, social, and political realities, he said, requires local handling. But state and federal overview is required in the interest of uniformity. "The translation of optimum environmental action requires local handling at county or lower level," he said. "However, federal and state overview may be required to assist in achieving minimum acceptable action that is beyond local resources and in the interest of uniformity."

Talks. Sen. Hollings and Commerce Secretary Dent were highlights of the meeting

Taking the point of view of the petroleum industry, Wayne Gibbens, president of Mid-Continent Oil and Gas Association, said that the national interest referred to in the 1972 Act is really the balance of many interests, including that of the petroleum industry. He said it was in the best interest of the nation to go ahead with offshore production of oil and gas, with increasing refinery capacity in coastal areas, and the development of deep water petroleum terminals.

Gibbens said that since oil production from land areas in the U.S. is "in a declining trend," and its future potential for further discovery is limited, "The frontier of American sufficiency lies immediately seaward of the coastal zone." A first goal should be to stabilize public policy with regard to the siting of petroleum refineries. These refineries should be built on the Atlantic coast near the high-consumption markets of the seaboard's metropolitan areas, he said.

Gibbens added that the U.S. will have to continue importing vast quantities of crude oil despite efforts to become self-sufficient. This activity necessitates the construction of deepwater ports. He presented figures that estimated imports on the Gulf Coast will have to increase to about 3 million barrels per day (bpd) by 1978, and on the East Coast to about 2 million bpd if future needs are to be met.

Environmentalists' viewpoint

On the environmentalists' side, Elvis Stahr, president of the National Audubon Society, said the real national interest demanded that ill-planned development along coastal areas be controlled. He said each state should be required to put into its coastal zone laws requirements for environmental impact statements, and that these statements should contain an examination of alternatives as well as the effect of new development upon the environment. He added that the financial positions of local planning officials involved in decision making should be revealed.

In the long run, the recent Council on Environmental Quality's report—"The Effects of Oil and Gas Drilling on the Outer Continental Shelf" (OCS)—should partially buffer the efforts of those who advocate an all-out development of these resources. The report concludes that leasing and development undertaken in the Atlantic OCS or in the Gulf of Alaska should be guided by a set of essential principles, which are stipulated in the report. The council claims that environmental risks can be minimized if such guidelines are followed.

The CEQ study points out that the risk of environmental damage varies from area to area. For example, development of the Georges Bank (off Massachusetts and Rhode Island) and the Southern and Central Baltimore Canyon (off Southern New Jersey and Delaware) would involve relatively lower environmental risks than development in the Southeast Georgia Embayment (off the Carolinas and Florida) and the Gulf of Alaska. The council concluded that when the environmental balance is unfavorable, development should not move ahead. Members questioned whether some areas should be developed at all.

Barbara Heller, from the Environmental Policy Center (Washington, D.C.), concluded her talk by calling attention to other development proposals for the coastal zones as well as offshore drilling. She said offshore nuclear plants, refineries, superports, platform fabrication facilities, and nonenergy-related activities such as sand and gravel dredging operations and hard mineral mining, all must be considered. The decisions for development should be joint ones, she said, the decisions to use up our natural resources should be made with care, wisdom, and concern for future generations. WSF

Environment and economic growth

The Committee for Economic Development believes that environmental improvement and economic growth can go hand in hand with proper cost/benefit planning

How can programs for a clean environment be made more effective? This question has caused much soul-searching in many quarters of industry, government, and academe. It is the subject of intensive study on the part of the Committee for Economic Development (CED, New York City), a business-academic organization of very high prestige, composed of leading, distinguished representatives of the industrial, economic, and university sectors.

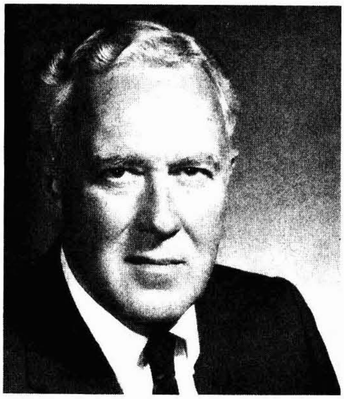
CED's study, conducted by the Subcommittee on Improving the Quality of the Environment (SIQE), chaired by Robert Semple, chairman of the board of BASF Wyandotte Corp. (Wyandotte, Mich.), stressed that:

- There will be a steady increase in the economical recovery of solid waste for fuels and materials, even if the energy shortage lessens.
- Despite uncertainties arising from fuel shortages, the U.S. can afford and achieve a high-quality environment if it adopts programs that weigh costs against benefits to produce maximum effectiveness.
- Although an economy that does not affect the environment is impossible, environmental progress will require more—not less—economic growth to carry the cost of pollution control (PC) programs.

Published this April, their study, "More Effective Programs for a Cleaner Environment," is billed as A Statement on National Policy by the Research and Policy Committee of the Committee for Economic Development. It cautioned, however, against "crash abatement programs."

Clean water questions

The 1972 clean water law amendments introduced great uncertainty into most major business investment decisions. Business cannot predict how the 1977 and 1983 guidelines and the stated zero discharge (ZD) goal of 1985 will be interpreted, or whether new or expanded plants will meet legal requirements. Protracted negotiations with officials and appeals to courts could come about.



CED's Semple

"ZD achievable if industry stops"

The subcommittee points out that the 1972 law requires uniform percentages of discharge abatement, which is very costly. Enforcement, with at least 50,000 permits needed, places a massive job of central planning in government hands and requires a large bureaucracy. This bureaucracy would be ineffective for lack of detailed price, market, and technology information available only to cognizant operating management. Thus the CED/SIQE foresees either lack of vigorous enforcement or widespread government regulation of business decisions.

The subcommittee therefore recommends a regional agency for each river basin or shoreline stretch to plan, execute, and control all public water-quality programs. This agency would enforce regulations, supervise federal grants, and conduct research. Each regional agency would differ in terms of responsibility and organization, depending on the region's needs. According to the CED/SIQE, the Delaware River Basin Commission comes closest to being such an organization.

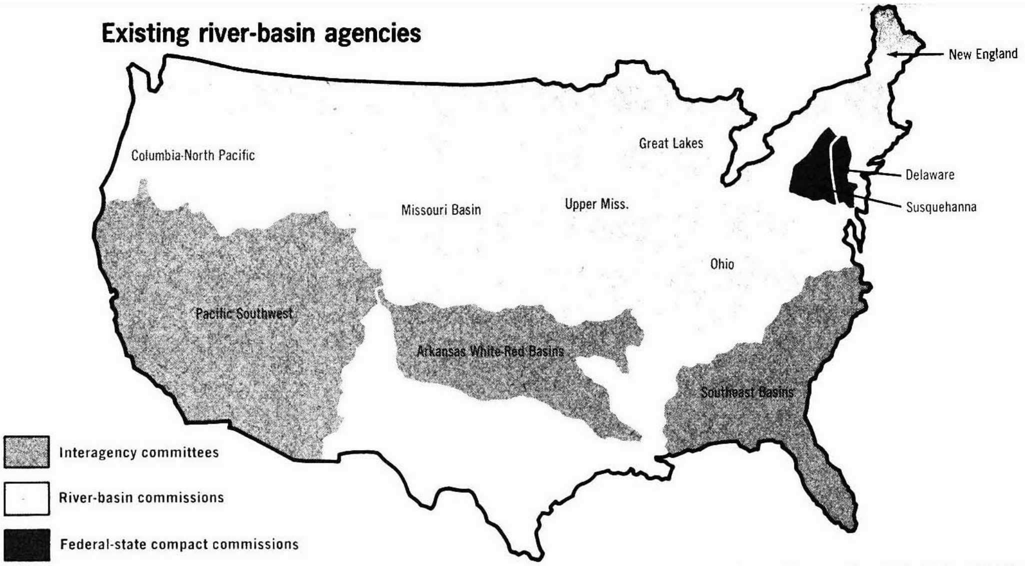
As an alternative to regulation, the subcommittee calls for the use of effluent fees in the form of a monetary charge per unit of waste discharged. Careful regulation of toxic discharges would be retained. This system is used rather widely in Europe, especially in Germany's Ruhr Valley where it has been in force for decades. The effluent fee system would put PC decisions in private hands, with incentives to seek economic PC methods, and make water quality improvement cheaper than would a system for direct regulation. Moreover, it would reduce the likelihood of discriminatory actions on the part of public officials, and remove much decision-making uncertainty.

The effluent fee concept, however, is not unopen to question. Du Pont president Edward Kane warns that the effluent fee is really a regulation under another name, and that payment of the fee would be considered by many as a license to pollute. This pollution might occur if fee payment is more economical than are controls. Charles Bowen, Jr., chairman of Booz, Allen & Hamilton, Inc., and Elvis Stahr, president of the National Audubon Society, emphasize that effluent fees must not be used (or misused) as a revenue source. Rather, reduction in fee proceeds should be viewed as a measure of PC success.

Into the air

To help allay uncertainties arising from the 1970 Clean Air Act amendments, Semple's CED/SIQE recommends air quality regions and regional agencies similar to those for water quality, with sufficient geographic flexibility to match PC with needs. The subcommittee also says that while an air emission fee system may be difficult to establish at present, ways should be sought to test the feasibility of economic incentives, similar to effluent fees, for regulating air quality programs.

With respect to air standards, the CED/SIQE strongly urges that envi-



Existing river-basin agencies

Source: U.S. Water Resources Council (Washington, D.C. 1972)

ronmental agencies carefully consider whether extremely stringent emission standards under very tight time frames, including those for motor vehicles, can be justified on the basis of cost-benefit comparisons. In view of the energy crunch, the Congress may be having the same thoughts. The Senate approved a delay from 1975 to 1977 for autos to conform to prescribed standards. Use of coal, where other types of fuel are not available, would be approved provided air quality standards are not being violated, or would be violated by conversion to coal. As this goes to press, differences between the Senate version, and a much more far-reaching House-passed measure, must be resolved at conference.

Solid wastes

The subcommittee recommends that the states should establish regional agencies to collect and dispose of solid wastes, since this effort is basically a problem of organization, rather than cost or technology. These regional agencies may be able to handle solid wastes at lower cost, with better enforcement of disposal, health hazard, and air and water PC requirements. Lower cost and improved services would be accentuated through increased reliance on private enterprise and its business competition.

The open dump, at which 75% of all municipal solid waste is deposited, must disappear, especially in large urban areas. The CED/SIQE calls for state and local governments to "take immediate steps" to substitute sanitary landfills and other disposal methods. In this regard, the State of Connecticut has a model system planned (*ES&T*, Sept., 1973 p. 802). If the cost is not justified, well-operated public dumps should be provided.

As things stand at present, however, enforcement of solid waste regulations is generally lax. In some states and communities, enforcement of laws already "on the books" is needed. In others, existing laws may need to be tightened. The subcommittee feels that if a locality is hard pressed financially, perhaps the state should share the cost of environmental upgrading required of these localities.

Frazar Wilde, chairman emeritus of Connecticut General Life Insurance Co., feels that the way things stand, the CED/SIQE proposals on solid waste will not be implemented, even in 25 years, if ever. He believes that states must be directly involved in the direction and financing of a solid waste program, mandated by state legislation, and set up on a regional basis. If enforcement consists of mere exhortation, many towns will postpone, procrastinate, or fail to participate in such programs. Federal grants should be made, Wilde believes, not only to develop and improve technology, but to help reduce costs through salvage coming from recycling.

Zero discharge

Zero discharge can be achieved almost overnight. Semple said that ZD could be attained if his company, BASF Wyandotte Corp., ceased all operations, and all other industrial municipal, governmental, and general human activity followed suit. The ultimate in ZD could be reached through cessation of breathing, and all other human, animal, and plant functions. Effects on the U.S. and world economy would probably not be altogether beneficial.

ZD is really grist for newspaper copy, and for certain politicians gathering votes. As Semple puts it bluntly, ZD is probably impossible to attain with present and anticipated technology and economics. Requirements for ZD stemmed more from emotionalism than from economic and technical good sense. One extreme example given by Clinton Allen, president of Wyandotte Terminal Railroad Co., and a very close associate of Semple's, is a requirement in some parts of Louisiana that an industrial plant return Mississippi River water "cleaner" than it was when it entered the plant.

Indeed, much discharge does little or no damage, as Semple points out, and the environment has a tremendous capacity to absorb discharges and dilute them to the vanishing point. To be sure, a factory could pollute a trout stream woefully, but the same factory's properly controlled discharges might be virtually unnoticeable in the Mississippi River. In the air, for example, a small, controlled amount of SO_2 (about two thirds of which is actually contributed by nature) is not dangerous. Indeed, to a certain extent, forests and grains need it for their normal growth.

Thus, the CED/SIQE cautions against tying environmental improvement into a reversal of economic progress. On the contrary, environmental improvement and economic growth could go hand in hand. Indeed, they must, for economic stasis or regression could have highly adverse social effects. Semple points out, however, that the environment is a resource whose use, like the use of all other resources, must be paid for, and it will be the consumer who ultimately pays the cost. JJ

The old town dump is obsolescent

People react negatively to trash and garbage. However, the value of recovered resources will help to alleviate a good part of the momentary olfactory irritation

The town dump quietly festering on a hot summer day—the city incinerator belching forth its rich, aromatic smoke as potentially valuable resources are uselessly wafted into the air—these landmarks may soon be consigned to the nostalgia file. To be sure, recycling and reuse of certain materials, particularly metals, is not new. Nevertheless, until recently, this type of resource recovery stayed largely in the category of "things that ought to be done." For the most part, it was simply less economical to use and reuse than to use and lightly toss away to the tune of 360 million tons/year.

The "three E's"—environment, energy, and economics—are rapidly changing this picture. Environmental cleanup necessities, together with increasing scarcities and skyrocketing prices of many prime materials, and improved techniques for solid waste processing, are bringing home the realization that "There's gold in that thar trash" (sometimes literally!). Recovering that "gold"—steel, aluminum, gas, oil and other values—was the topic of concern at the National Materials Conservation Symposium (NMCS, Gaithersburg, Md., April) and the Fourth Mineral Waste Utilization Symposium (4th MWUS, Chicago, May).

The NMCS was sponsored by the National Bureau of Standards (NBS), U.S. Bureau of Mines (BuMines), EPA, National Center for Resource Recovery (NCRR), and American Society for Testing and Materials (ASTM). The 4th MWUS was sponsored by the Illinois Institute of Technology Research Institute (IITRI) and BuMines.

Garbage power

At the 4th MWUS, Fred Steffgen of the BuMines Pittsburgh (Pa.) Energy Research Center, described some means by which organic refuse might be converted to fuel oil or gas. One such means is the BuMines CO-steam process in which organic waste slurry, together with recycle oil, is reacted with carbon monoxide (CO) and steam, with catalysts, under high temperature and pressure. A 3000-tpd plant could make 632.8 tpd of oil (14,400 Btu/lb heating valve) and 75.8 tpd of ash which can be burned for heat, as can excess synthetic gas and off-gas, which are also produced. Oil potential is estimated at 40–41% by weight of moisture- and ash-free (maf) waste.

Typical steel scrap
(% impurities)

	Aluminum	Chromium	Copper	Molybdenum	Nickel	Tin
Auto	0.03	0.13	0.21	0.015	0.11	0.02
Raw refuse	1.8	0.08	0.10	—	0.04	0.43
Incinerated refuse	0.5	0.10	0.41	—	0.09	0.15
Reject can mix	3.3	0.05	0.06	—	0.03	0.49
Maximum desired	—	0.03	0.06	0.01	0.03	0.01

Source: Paper by C. Daellenbach, 4th MWUS (BuMines/Salt Lake City, Utah).

The BuMines Hydrane process, and the Institute of Gas Technology (IGT, Chicago) Biogas process are aimed at producing pipeline-quality substitute natural gas (SNG). In the Hydrane process, organic waste is treated at 1000 psi pressure, 550–700° C, and gasified. Oxygasification and steam treatment of char provide the hydrogen for the methanation step. Gas yield could be 53–63% by weight, based on organic carbon, or over 19 million ft^3 of gas per ton of waste. Pyrolysis at 900°C, by comparison, might give over 15 million ft^3 of 550 Btu/ft^3 gas per ton of waste.

IGT's Donald Klass estimated that 204 million tons/year of municipal refuse are currently produced in the U.S. This refuse could provide about 1 trillion ft^3/yr of SNG which can be economically evolved through the Biogas process which uses anaerobic digestion of a refuse-sludge feed, and is being tried with Indianapolis refuse. Organic residue can be disposed of without undue ecological abuse. Similar processes are being tried in Israel and other locations (*ES&T*, February 1974, p 105). However, heavy metals and grit should be separated, preferably before digestion.

Direct burning of organic garbage is another approach to energy recovery. Union Electric Co. (UEC, St. Louis, Mo.) is replacing 10% or more of the pulverized coal used in some boilers at UEC's Meramec plant with burnable garbage. Solid waste and ash analysis, emission and corrosion testing, and boiler performance observations are not as yet complete, but results to date appear very encouraging. A similar approach is being tried in Spain.

Playing it cool

The billions of waste rubber tires are augmented annually in the U.S. by about 234 million additional junked tires. "Piled one on top of the other, these waste tires would reach the moon," Norman Braton of the University of Wisconsin/Madison, said. Moreover, these tires cannot be burned, buried, or biodegraded.

Braton's approach is to spray these tires with liquid nitrogen after they are cut up. The rubber becomes very brittle, and is pulverized; clean fabric or metal values from the tire are then easily recovered. Tire volume is reduced by 80%, which is significant, since tire shipping costs are about $15/ton. One ton of tire rubber can be retorted to give 1500 ft^3 of gas and 150 gal of oil; the remaining residue makes a good filter, asphalt mix, or soil conditioner, and has even been found to filter mercury from stream water. Cost of cryoprocessing of tires is estimated at 10–20¢/tire, as opposed to $1.00/tire by "conventional" means; moreover, marketable products are obtainable.

Old wires, aluminum and steel cables, plastic extrusions, scrap telephones, similar wastes can be cryoprocessed. Paint, insulation, plastic, and similar materials are easily removed, and clean metal is ready for the recycled materials processor. Cryoprocessing costs are determined by the temperature of the material before liquid nitrogen treatment, and by the manner of conveyance of the material through the treatment system.

J. Bilbrey, of BuMines/Salt Lake City, estimated that 600 lb of liquid nitrogen will handle one ton of scrap metal; with more efficiency, liquid nitrogen requirements could be lowered to 300 lb. For certain nonferrous recovery applications, such as copper–zinc scrap, zinc recovery has been found to be almost quantitative, since zinc shatters when very cold, but copper does not.

Estimated "garbage power" costs

Process	Product	Amount, per ton of waste	Capital costs	Operating costs, dollars
CO-steam	Oil, 14,400 Btu/lb	422 lb	$51.2	$9.48/ton waste 7.86/bbl oil
Hydrane	Gas, 1,000 Btu/ft^3	19.6 million ft^3	16.9	2.13/ton waste 0.45/100 ft^3 gas
Pyrolysis	Gas, 550 Btu/ft^3	15.7 million ft^3	9.7	3.13/ton waste 0.50/1000 ft^3 gas

Source: Paper by F. Steffgen, BuMines/Pittsburgh, Pa.

Mine and mill waste

If the chemical composition is right, certain furnace clags and mine or mill tailings may have good value in a number of markets, particularly as construction materials. By "right" chemical composition, it is meant that lime may not exceed silicate by more than 10%, or the material could easily break down. Steel slag is often recycled back to a steel plant; however, blast furnace slag could have a variety of structural uses. Certain mine and mill tailings may also prove useful as building materials, but sometimes slight radioactivity may mar the tailings' utility, as in the case of uranium tailings, or some dewatered phosphate slimes.

In the Soviet Union, a building material called "temoseryy shlakositall" was developed from metallurgical slag. This "shlakositall" has a bending strength of 1200 kg, and a compression strength of 7000 kg, and it can withstand an impact of 7 kg-cm/cm^2. The Russians hope to market this material worldwide through their patent licensing agency, "Licensintorg."

One of the prime reasons for using slag, tailings, or fly ash is to try to substitute for or replace portland cement. Some of these materials may also be good for paving as well as building, and have acceptable wearing, antiskid, and antistripping properties. If these slags or tailings have sufficient fines and amorphous material, as well as a minimum of lime or alkali, they could become a constituent of building materials, such as pelletized slag bricks, meeting ASTM specifications, and sometimes being equivalent to 25,000 psi concrete.

Recycling metals

Ferrous and nonferrous scrap is derived from numerous sources. In some cases, the scrap is fairly pure, as in the case of aluminum cans or battery lead. Aluminum cans, for example, need only be cleaned, melted down, and reformed into acceptable ingot with 5% of the energy expenditure needed to obtain primary aluminum.

When ferrous or nonferrous metals are mixed or alloyed, however, metal separation will present varying degrees of difficulty. For instance, in the previously mentioned cryoprocessing, zinc, a scarce resource, can often be quantitatively separated. In the case of metal from the ubiquitous junked electrical appliance, tin can, or car, a far more difficult situation is encountered.

The car, particularly, presents some tough problems. Elliott Estes, executive vice-president of General Motors Corp., told the NMCS that 80–85% of all retired vehicles do get into the scrap recovery network with no problem. However, there are 15 million auto hulks rusting outside this network, and 400,000 more being simply abandoned each year. To make things worse, Estes says, many states make it legally cumbersome or impossible to "de-title" such derelict autos; moreover, the present rail freight rate structure discourages wider use of recycled or reclaimed material.

Technical problems exist, too. C. Daellenbach of BuMines (Twin Cities, Minn.) told the 4th MWUS that typical auto scrap steel may contain 0.03–0.11% aluminum; 0.13% chromium; 0.21% copper; 0.11% nickel; and 0.02% tin. Moreover, there is 3.72% carbon, 1.94% silicon, and 0.077% sulfur. Varying amounts of these materials, some deleterious to steel strength, will also be found in metal from raw refuse, incinerator residue, and reject cans.

One approach to separating objectionable metals, by vacuum melting in an induction or electron beam furnace, was announced by the Atomic Energy Commission (*ES&T*, January 1974, p 11). Then, upon addition of correct amounts of nickel and chromium, a No. 304 stainless steel results. Another approach, used by BuMines/Twin Cities, was to melt the scrap at 2530°F with a scrap–coke ratio of 5.5:1.

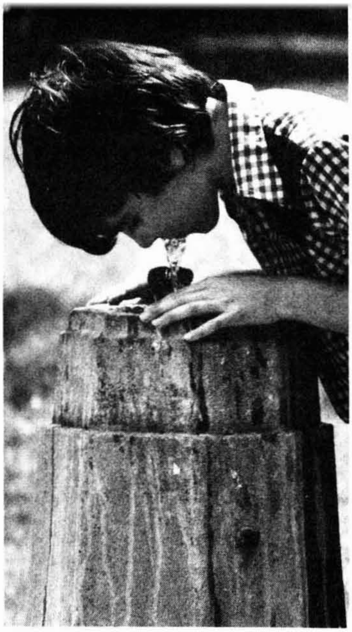
Gerald Grott, president of Western America Ore Co. (WMOC, Coolidge, Ariz.) proposed a single-step melter furnace to convert auto scrap to refined steel by using the furnace as a sophisticated chemical reactor. Grott's idea, based on long experience, is to remove tin, and substitute copper for a portion of the nickel in low-alloy steels. The quality would not be impaired. Nonferrous dust and fumes would be captured in a baghouse, refined, and marketed at a profit at present prices. Enough waste heat would be generated to contribute substantially to all electric power needed for the process, Grott said.

For an operator able to handle 150,000–300,000 auto bodies/year, Grott estimated that a furnace, preheater, baghouse, and laboratory/data center would cost $2.44 million. Operating costs (200,000 cars/year) would be about $15.30/ton, and annual personnel costs $1.2 million. These costs would be far less than those of "conventional" approaches, in which a 100-tpd shredding plant costs over $2 million, conversion costs vary widely around $10/ton, and electric melting costs run $22–26/ton exclusive of metallics and costs listed above.

Goodbye, town dump!

Demand for materials will continue to soar, environmental regulations will become more stringent, and severe world competition for raw and primary materials, with concomitant price escalation, will result. Thus, recycling and reuse of materials will take their proper place in the industrial economy. Part of the cost of the technology needed to achieve this aim might be defrayed by the value of hitherto unused research, which WMOC's Grott told the 4th MWUS "is bigger than the national debt."

Goodbye, town dump! You will not be missed. JJ



How pure is our water supply?

Some feel that water pollution is not detrimental to our health; others call for money and technology to better water quality

Conditions of the water utilities in the U.S. are only good compared with underdeveloped countries, according to an EPA official at the 7th International Water Quality Symposium held last April in Washington, D.C. F. B. Taylor illustrated his point with the results of a 1969 study:

- 36% of the tap water sampled contained too much bacteria
- 56% of the water systems had deficient plants
- 77% of the water works operators were inadequately trained
- 79% of the utilities had gone through a year without a state or county inspection.

The director of the American Water Works Association, E. F. Johnson, felt that public ignorance had contributed to the sloppiness on the part of the utilities. He believed that if the public knew how little it would cost for high quality water, and thus demanded better water, the utilities would have to do more than just the minimum.

But in Europe, water conditions in densely populated and highly industrialized areas are even much worse. Some 40 million people are drinking water from the polluted Rhine River, according to one of Europe's leading water utility managers. It is hoped that the river will be cleansed in the next 10–15 years.

U.S. use and supply

Water consumption has soared from 40 billion gpd in 1900 to 390 billion gpd in 1968. By the year 2000, the projected needs will be 1000 billion gpd. Home usage has been mainly for toilet flushing, bathing, and laundering. Elsewhere, water is used for heating, cooling, cleaning, and as a solvent.

Over 90% of our freshwater resources is underground. Yet only 20% is extracted for our supply, pointed out Jay Lehr of the National Water Well Association. He felt that groundwater is a valuable source sufficient to last 7000 years or more at the current depletion rate. Comparing costs—13¢ per 1000 gal for surface water, 5¢ per 1000 gal for groundwater, and 30¢ per 1000 gal for desalted water—he questioned the preference for surface systems, such as lakes and dams.

The rebuttal came from D. W. Miller, a geologist, who said underground sources are being threatened by contamination. He listed septic tanks, land fills, fertilizers, pesticides, unlined industrial waste lagoons, and ruptured oil tanks as the polluters.

Pollution

And yet water pollution, at present levels, has little direct effect on our health, and "virtually none" on death rates, asserted E. A. Lew, president of the Society of Actuaries.

In fact, trace elements, like chromium, are important in our nutrition. For example, the hexavalent state of chromium occurring in water is much better absorbed by the human organism than the trivalent form present in foods, noted Walter Mertz, chairman of the Nutrition Institute of the U.S. Department of Agriculture. Some trace elements are also preventive against cardiovascular diseases, explained a specialist in the heart field.

On the other hand, water purification is still necessary for better quality, said K. E. Shull, an executive with the Philadelphia Suburban Water Co. He did not think that chlorination, the only treatment method used by about half of the community suppliers of water, was effective in removing pesticides, herbicides, and other organic and inorganic chemicals. For better treatment, he thought that the public should pay higher rates.

Thinking along the same lines, Associate Justice W. O. Douglas of the U.S. Supreme Court calls money the key to water purity, and a stimulant to better technology.

Closing the loop

To achieve the national goal of zero discharge of pollutants to its navigable waters by 1985, as established by the P.L. 92-500, will require the recycling of industrial process wastewaters, said N. C. Kachman, manager of General Motors Corp.'s Plant & Engineering Group.

In closing the influent/effluent gap, there is the problem of dissolved solids removal on a "practical and economical basis," he went on to say. At GM, three reverse osmosis configurations for dissolved solids removal are undergoing evaluation.

GM is also considering the aspect of the ultimate disposal of the dissolved solids, within the concentrated state. The assumption is made that dissolved solids can be removed effectively and economically from the effluent stream to permit the reuse of water. In some cases, the concentrate may be satisfactory for use as a flushing medium for water closets and urinals prior to discharge to the sanitary sewer. In other cases, such as a concentrate containing high concentration of metals, it may be feasible to evaporate the stream and recover the metals.

An important consideration to water conservation efforts is that perhaps the resulting savings in energy costs cannot be offset by the higher energy requirements imposed by the zero discharge goal. LCG

Thirty-one industries whose wastes are emptied into municipal systems, are now required to comply with . . .

Pretreatment standards for discharge

Discharge of industrial wastewaters into combined municipal sewer systems has, in the past, been fairly unregulated. Industries, often with neither the available space nor the accessible waterways, have found it necessary to use the publicly owned wastewater treatment plants. Up to now, the extent of their on-site treatment has only been affected by local ordinances and user charges assessed by the municipals.

With the advent of tougher effluent standard, urban areas have had to limit the pollutants industries can introduce into their treatment systems. Thus industries will have to be more rigorous in pretreating their wastes to be compatible with their respective municipalities.

Earlier, pretreatment guidelines for pollutants entering waterways had been developed by the federal government. Now, pretreatment standards are being promulgated for 31 industries. This month is the cutoff date for promulgation of all standards for these industries.

Pollutants

Allowable industrial wastes are by definition compatible pollutants, that which will be removed by the particular treatment processes employed by the particular municipality. Because they are removed, they will not harm or adversely affect the operation of the municipal treatment plant and its ability to meet effluent criteria.

Examples of compatible pollutants include biochemical oxygen demand (BOD), suspended solids (SS), pH, and fecal coliform bacteria. Pretreatment of wastewaters containing these and other compatible pollutants may sometimes be necessary, for example, in the form of spill protection or flow equalization.

On the other hand, specific prohibited wastes listed by the EPA encompass wastes which are inflammable, corrosive to the plant's structures, obstructive to the sewer's flow and have excessive flow or discharge rate.

Pre- and joint treatment

The EPA requires that major contributing industries pretreat their incompatible pollutants with the best practicable control technology. By definition, a major contributing industry is one that has:

- a flow of 50,000 gpd
- a flow greater than 5% of flow carried by the municipal system receiving the wastes
- amounts of incompatible pollutants in violation of standards issued under Section 307 a of the P.L. 92-500
- a significant impact, singly or in combination with other contributing industries, on the public works.

Available pretreatment techniques vary from biological to physical-chemical. The former covers the aerobic lagoon, roughing trickling filter, and anaerobic systems. The latter includes such processes as screening (to remove coarse particles), sedimentation (to remove SS), equalization (to minimize fluctuations in wastewater characteristics), neutralization, and dissolved and induced air flotation (to clarify or thicken).

Joint treatment of industrial and municipal wastewaters is recommended by the EPA. A case in point is the discharge of industrial wastes containing organic material but devoid of nutrients required for biological treatment. If joint biological treatment is used, nutrients need not be added since they are already present in the municipal wastewaters.

Sampling

To be sure, sampling techniques and equipment will differ with the individual requirement of a particular industry. Nevertheless, grab samples are generally recommended for analysis of dissolved gases, residual chlorine, temperature, pH, and soluble sulfides. Composite samples are taken for monitoring flow variations, perturbations in waste constitutents, and the like.

Manual sampling is good for a preliminary survey of the conditions, whereas automatic sampling is more convenient in separate treatment schemes for specific process wastewaters. The frequency of sampling should be dependent on the flow rate, wastewater characteristics, and the parameters to be monitored.

In any event, a comprehensive sampling program should save time and facilitate industries whose date of compliance is set at no later than three years from promulgation, and who should begin building required pretreatment facilities within 18 months from promulgation. LCG

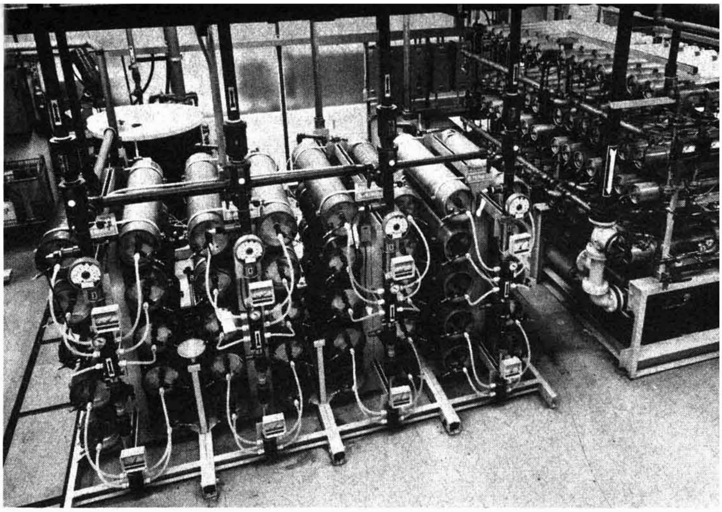
Pretreatment requirements for discharge into municipal systems

	LIMITATIONS			
Constituents	**Dallas, Tex.**	**Evansville, Ind.**	**Cincinnati, Ohio**	**Chattanooga, Tenn.**
Temp, °F	150	—	150	—
Oil and grease,[a] mg/l.	100	—	100[b]	100[b]
pH	>5.5, <10.5	—	>5.5, <9.5	>5.5, <9.5
Chromium, mg/l.	3	5[c]	5[c,d]	5[d]
Copper, mg/l.	3	3[d]	3[d]	3[d]
Zinc, mg/l.	3	2[d]	2[d]	2[d]
Nickel, mg/l.	3	—	—	—
Cadmium, mg/l.	3	—	—	—
Iron, mg/l.	3	15[d]	15[d]	15[d]
Lead, mg/l.	—	—	—	—
Cyanide, mg/l.	3	2	2	2
Radioactivity, μc/l.	100	—	[e]	—
Chlorine demand, mg/l.	—	30	30	—
BOD, mg/l.	—	[f]	—	—
H_2S, SO_2, N_2O, mg/l.	—	—	10	10
Phenol, mg/l.	—	—	0.5	0.5

[a] Free and emulsified substances. [b] Substances highly viscous 32–150°F. [c] Hexavalent chromium only. [d] Concentration of total waste flow influent to treatment plant. [e] Substances with half-lives >100 days. [f] Peak concentrations for 15 min or longer limited to 5 times normal sewage BOD and SS concentrations.

Source: AWARE, Inc. (Nashville, Tenn.).

FEATURE



Finding the right pretreatment process—by the continuous operation of a pilot plant before full-scale construction—provides . . .

Reverse osmosis treatment with

Lional B. Luttinger and Gabriel Hoché
The Permutit Co., Paramus, N.J. 07652

The membrane process considered here is essentially reverse osmosis (RO). Other membrane processes, such as ultrafiltration and the various types of electrodialysis, have been coming into commerical use. The latter processes share many of the same pretreatment problems with RO, but may involve different pretreatment problems arising from the electrochemical processes involved in electrodialysis, for example.

Primarily, RO pretreatment problems arise from seawater and brackish water desalination as well as other types of applications. With regard to pretreatment for RO systems, the type and extent of such pretreatment depends on a number of factors:

- the type of RO equipment used
- the extent of conversion desired; for example, how concentrated a reject stream is to be produced
- the type of water treated
- the desired quality of the end RO-treated water.

RO considerations

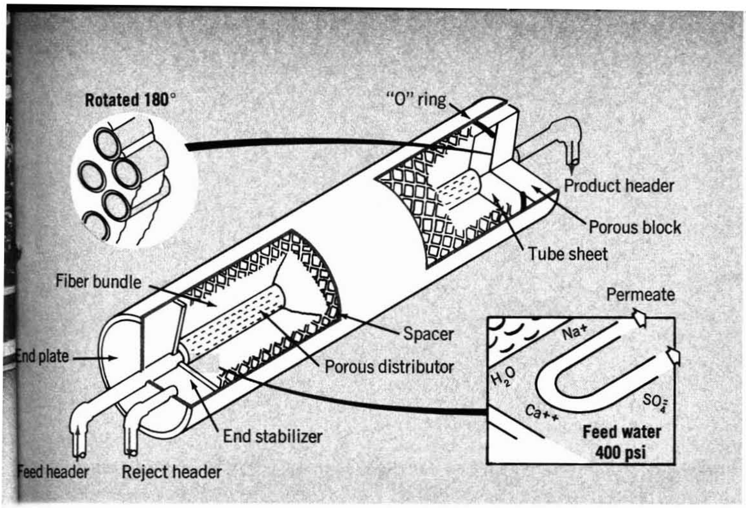
The major contemporary types of commercial RO equipment (tubular, spiral wound, and hollow fiber) each have individual idiosyncrasies with regard to the optimum pretreatment they require. For example, cellulose acetate membranes are highly pH-sensitive and are best used in the pH range 5–8. The polyamide membranes used in the Du Pont B-9 hollow fiber permeator are much less sensitive to pH, but more sensitive to certain other chemical additives such as chlorine.

In RO water treatment, the materials rejected by the membrane will concentrate in the reject stream. Since, in many cases ($CaSO_4$, $CaCO_3$), an untreated RO influent is already saturated or nearly saturated with respect to such species, the inevitable further concentration in the RO module results in exceeding the solubility products of such species, resulting in precipitation with the likelihood of plugging or fouling the module. At relatively low extents of conversion (50%), the Langelier index, the kinetics of precipitation, or high linear throughput velocities in the module may all tend to keep precipitation from occurring in the module. However, at higher conversion rates, say, 75%, when the dissolved solids in the reject stream are concentrated fourfold and other things remain unchanged, precipitation probably occurs in the module.

In many cases, such precipitation can be prevented by adjusting the pretreatment regimen so that the Langelier index of the reject stream will still be "safe" (zero or slightly negative). For the calcium salts considered above, softening, desulfating, pH adjustment, and addition of sequestrants are examples of pretreatment steps that will permit RO operations at higher conversions without the danger of precipitation/fouling in the module. In the case of lower extents of conversion, such pretreatment might not be necessary or might be required to a smaller degree. Similarly, fouling by other materials such as colloids and organics constitute much more serious problems at high, and not low, extents of conversion.

Various types of water can be treated via RO and other membrane processes. The particular water will, to a large extent, determine the type of pretreatment desired. At one end of the scale are certain well waters and some already "refined" waters such as adequately treated municipal waters, which may require little or no further pretreatment. On the other end, some surface waters, even after clarification and other municipal treatment to reduce suspended solids to very low levels, have been notorious for the trouble they can cause when used directly in RO without further pretreatment. Seawater, which is high in hardness, particulate and colloidal matter, corrosive chloride ion, and a wide variety of "trace" compounds, presents special pretreatment problems.

At the far end of the scale are those waters containing large quantities of solids or which require special sanitary handling. Such waters comprise certain chemical waste streams, process chemical streams, foods, pharmaceuticals, and municipal sewage. They may require special pretreatment regimens, as well as special module geometries and special flow velocities and/or turbulence promoters, in order to prevent fouling, and may sometimes require the use of special materials of construction as well. Surface or seawater may be made more suitable for RO applications by means of a Ranney or radial water collector system, consisting of a series of screened horizontal lateral porous pipes radiating from a central cais-



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son set close to the water supply. This system functions as a deep bed earth filter.

To some extent, pretreatment will determine the quality of the effluent through a membrane system. For example, certain gases (oxygen, carbon dioxide, hydrogen sulfide) are not well rejected by most RO membranes. If low values of such species are required in the effluent, these gases may be removed in a pretreatment step, such as degasification, pH adjustment, or in a post-treatment step of the same type. Similarly, if an RO system can remove, say, only 90% of the ions in the influent, and a much greater level of removal (99%) is required, pre- or post-treatment (ion exchange resins) will represent one method of achieving this result. Another method consists of "staging" the RO modules.

Membranes are also subject to mechanical imperfections which permit the passage of small quantities of colloids, bacteria, and viruses. In many cases, even small quantities of such materials are highly undesirable in the RO effluent and must be removed by pretreatment.

Treating water contaminants

Particulate (suspended) matter occurs to some extent in all waters. Some material of this type is unobjectionable in small quantities in many installations. More commonly suspended matter causes problems such as increased wear on the pumping system, fouling of the membranes, and transport of bacteria, viruses, and other finely divided matter through the system. For these and other reasons, almost all RO systems are protected by some type of cartridge filter whose function is to remove such material. Filters are often of the spool-wound fiber or paper type but may also comprise membrane filters. Usually, they are designed to remove particulates larger than 5–25 μ from the influent water. Finer membrane filters (removal of particulates above 0.2–0.45 μ) are also used in some installations. In treating thick pastey liquids such as tomato paste and concentrated wastes, a filter of this type may be replaced by a more open-textured grid to catch large particulates. The finer filters of this type will also remove some slimy material from many waters.

The concentration of **calcium** and **carbonate ions** in the RO reject stream leads, in many cases, to precipitation of calcium carbonate which can foul and damage the membranes. This concentration is particularly so where influent water or reject stream has a positive Langelier index. Deposition of this salt can, however, easily be prevented via several techniques of which, perhaps, the simplest is pH adjustment. At a pH of 5–6, the carbonate ion concentration is so reduced via bicarbonate formation that precipitation will usually not occur, save in the presence of very high levels of calcium ion. Other means of preventing calcium carbonate precipitation are hot or cold lime softening, ion exchange softening, and chelation or sequestration of the calcium ion. Since all these methods are relatively simple and foolproof, prevention of calcium carbonate formation constitutes one of the simpler pretreatment problems.

Calcium sulfate precipitation causes similar problems in RO modules. Pretreatment for prevention of calcium sulfate precipitation is more difficult, since this reaction is relatively unaffected by pH changes which constitute the simplest means of controlling calcium carbonate precipitation. Nevertheless, the various forms of softening mentioned under carbonate treatment may all be effective. In addition, ion exchange removal of sulfate ion via basic ion exchange resins is also possible. A number of chelants and sequestrants will also help prevent deposition of massive calcium sulfate in the RO module.

Iron and **manganese** behave rather similarly in water and RO systems and are removed via similar types of pretreatment. Their soluble (ous) forms are rejected by the membrane. Their higher oxidation states (hydrous ferric and manganese oxides), in the forms of particulate, colloid or slime, can deposit on the RO membranes and cause serious fouling. The chief danger here is oxidation to insoluble forms at or near the membrane.

Several effective means of preventing fouling by these ions are available. One means is oxidation followed by filtration. The ions are first fully oxidized to the insoluble forms and the latter are filtered out in a pretreatment step. Perhaps the most effective combined pretreatment of this type is manganese zeolite oxidation and filtration. In this method, the influent is passed through a finegrained filter bed of manganese zeolite oxidized with permanganate. Manganese and iron in the "ous" states are quantitatively oxidized to insoluble forms in the bed and are trapped therein, resulting in excellent removal of these materials from the water. The exhausted manganese zeolite bed can be regenerated, when required, with permanganate and can also be effectively backwashed as needed.

Iron and manganese fouling can also be prevented by reduction of the insoluble and colloidal materials to the soluble "ous" forms. This can be achieved by treatment with a reducing agent such as sulfite. Deoxygenation (degasification) of the influent can be employed to prevent oxidation of these ions. Organically bound iron and manganese are more difficult to treat than the inorganic forms. In such cases, the usual oxidation and filtration treatment of these metals may not be effective, and more powerful methods (use of higher concentrations of oxidants, adsorption on macroreticular resins or activated carbon) may be necessary.

Colloids frequently present great difficulties to an RO system. They are not effectively removed by most conventional filters due to their small size. Columns of activated carbon, which are often so effective in removing soluble organics from water, are often much less effective in removing colloids. Of the various types of colloids causing serious fouling problems, among the most difficult to pretreat are silica and clays, biochemically produced organics, and high polymers.

Among the more simple means that can be used for colloid removal are filtration assisted by coagulation/flocculation. In one variant of this method, a sand-mixed media or diatomite bed is pretreated with a very dilute solution of polyelectrolyte flocculant or freshly precipitated inorganic coagulant (hydrous oxides of ferric or aluminum ions), which deposits a coating on the filter that is relatively effective in collecting colloids. In another variant, the hydrous metal oxide or polymer, at very low concentrations, is fed continuously into the influent water to the filter (in-line coagulation). If proper concentrations, contact times, mixing, and the proper reagent are established, colloids as well as particulate matter may be largely removed from water by such processes. When larger (1,000,000 gpd) RO plants become commonplace, the additional cost of such treatment will be relatively small.

The use of a sludge blanket precipitator/clarifier constitutes another means of colloid removal. Particulate matter is also easily removed this way, and the pretreatment system may be run so as to precipitate and remove various other impurities (calcium sulfate, calcium carbonate, silicates, iron, manganese, microorganisms, polymers) at the same time. In the sludge blanket precipitator/clarifier, addition of chemicals is followed by thorough mixing. After a detention time sufficient for the various precipitation, coagulation, and flocculation reactions to occur, the contents of the precipitator/clarifier rise. Since the reaction vessel is shaped like an inverted pyramid, the actual rate of rise decreases as the fluid ascends. A final point is reached, partway up the reaction vessel, at which the sludge phase is stabilized. The sludge remains close to this position as a thick "sludge blanket" of suspended solids and semisolids, containing much colloidal matter. The clear water, meanwhile, passes through the blanket and out of the precipitator/clarifier to the RO system.

A properly operating sludge blanket precipitator can act as a trap for much colloidal matter which is caught in the blanket and will usually grow in particle size with time. The efficiency of the device with regard to colloid and particulate removal can be increased by recycling some of the mature sludge and installing chevron-shaped tube settlers. The latter permit the attainment of much faster flow rates through the system.

Colloids can also largely be removed from RO influent by a pretreatment step consisting of an ultrafilter. Ultrafilters pass virtually all dissolved material and can be operated at higher flow rates and lower pressures than RO

Typical Permu RO installations

Company	Market	Application	GPD
Arabian American Oil (Saudi Arabia)	Petroleum	Potable and boiler feed water	172,300
Bowmar Canada Ltd. (Ottawa, Canada)	Electronics	Process	24,300
Cavanagh Communities (Rotunda West, Fla.)	Municipal	Potable	500,000
City of Leeds (Leeds, N. D.)	Municipal	Potable	100,000
Eagles Point (Punta Gorda, Fla.)	Municipal	Potable	18,000
Gulf State Utilities (Beaumont, Tex.)	Utility	Boiler feed water	12,000
Kingston Shores (Ormond Beach, Fla.)	Municipal	Potable	172,800
Microsystems (Ottawa, Canada)	Electronics	Process	100,000
Mobil Oil (New Orleans, La.)	Petroleum	Potable	6,000
Monongahela Power (Haywood, N. C.)	Utility	Boiler feed water	360,000
Mostek (Carrollton, Tex.)	Electronics	Process	216,000
Nevada Power (Las Vegas, Nev.)	Utility	Boiler feed water	95,000
RCA (Mountain Top, Pa.)	Electronics	Process	18,000
Republic Steel (Cleveland, Ohio)	Metals	Waste	57,600
Salt River Project (Kyrene, Ariz.)	Utility	Boiler feed water	288,000
Southwestern Public Service (Earth, Tex.)	Utility	Boiler feed water	50,600
Sparkletts Drinking Water (Santa Ana, Calif.)	Municipal	Potable	60,000
Stelle Group (Chicago, Ill.)	Municipal	Potable	24,300
Unitrode (Watertown, Me.)	Electronics	Process	28,000
Yates Industries (Beaumont, Calif.)	Metals	Waste	60,000

Main reverse osmosis applications

Water treatment

Production of high purity water for use in electronics, power, and chemical process industries

Desalting brackish waters for municipal, hotel, and commercial use

Wastewater treatment

Treatment of plating and metal finishing wastes for recovery of metals and rinse waters

Tertiary treatment of industrial wastes such as textile, pulp and paper, and petrochemical

Tertiary treatment of sewage

systems. A relatively small ultrafilter can thus pretreat for a large RO installation. It is also possible to use RO membranes themselves as a pretreatment method for the bulk of the RO system.

Handling other contaminants

Dissolved organics, unlike suspended colloidal organic matter, are often not precipitable or coagulable, with the exception of long chain fatty acids and other weakly ionizable materials. A number of these soluble materials not only foul membranes, but can, in high concentrations, act to dissolve them in part.

In seawater pretreatment for membrane processes, soluble organics are not expected to prove a major problem, the overall concentrations of these materials in seawater being relatively low and constant and relatively innocuous with respect to membrane solubility and corrosion enhancement. Nevertheless, it may prove necessary in many instances to pretreat seawater as well as other waters for soluble organics removal. Oxidation with chlorine or hypochlorite will remove much of the soluble organic matter as well as some colloidal and particulate organic material. Stronger oxidants, such as ozone or permanganate, should prove even more effective to this end, but are more expensive.

Filtration through beds of activated carbon constitutes the other major means of removing most soluble organics. The spent activated carbon may be regenerated relatively cheaply in large scale operations. However, not all organics are adequately removed by active carbon treatment, and further treatment, for example, with an oxidant may also be required. Activated carbon beds can also be used to keep the chlorine residual from chlorine pretreatment down to levels that would not damage the RO membranes. Similar to the use of activated carbon is the use of macroreticular resins—organic traps. These materials behave similarly to active carbon beds in trapping organics. Macroreticular resins of various types are available. They offer the advantages of greater ease or regenerability and better mechanical stability than activated carbon. Although they are more expensive than the latter, they efficiently remove certain organic colloidal materials such as lignin derivatives, detergents, and humic acids which are less effectively removed by carbon.

Bacteria and their metabolic products can foul and also damage RO membranes. These microorganisms, together with viruses, may pose health hazards or cause undesirable contamination in certain applications. Algae represent gross particulate matter and may, together with their metabolic products, clog various parts of the system. All these materials are generally undesirable and should be removed. Algae themselves can be removed by filters such as sand filters and even microstrainers. Removal of such material at the far upstream end of the system prevents the development of complex problems farther down the line. All these organisms will be removed rather successfully by in-line coagulation, ultrafiltration, or by a sludge blanket precipitator/clarifier. In addition, all are easily destroyed by chlorination and other oxidative treatment which destroys other forms of organic particulate matter as well.

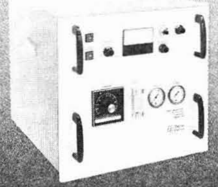
Silica and **silicates** may give rise to virtually irreversible fouling in membrane systems; hence their removal is important. Silica exists in water in several forms. Crystalline and amorphous colloidal silica are usually both present. Colloidal silica presents such special problems that it is discussed here, apart from other colloids. Some of the silica is in true solution form—H_2SiO_3 and others. The soluble forms of silica may, for a variety of reasons, polymerize in the RO system to form deposits and films. However, it is the amorphous forms of silica, including silicates (clays), which frequently cause the most trouble in RO systems. Such materials, particularly of submicron particle size and even at very low concentration levels, often give rise to a particularly refractory type of fouling that is difficult to prevent.

The crystalline, and to some extent the amorphous, forms of silica can be removed by coagulation in a sludge blanket precipitator. Coagulation can be achieved with ferric sulfate in conjunction with lime, at an optimum pH of about 9.0. The dosage required depends on the silica content of the raw water and the extent to which it is to be removed but, in general, it is rather high—about 8 to over 20 ppm of ferric sulfate for each ppm of silica removed. Amorphous silica can be, to a large extent, hydrolyzed with caustic to low-molecular-weight dissolved forms. Dissolved silica can be removed by ion exchange, by the cold lime–soda–magnesia or hot lime processes.

The removal of soluble silica by ion exchange can be accomplished by the use of a strong base resin in the OH^- form. Soluble silica can also be removed by magnesia in a cold lime softening process. It has been found that magnesium hydroxide is effective to this end. Therefore, the magnesium hardness of seawater, since it is precipitated in situ as magnesium hydroxide when lime or caustic is added, can be used to reduce the silica content. The sludge blanket precipitator is most commonly used for silica removal because a prolonged, intimate contact with an excess of magnesia-containing sludge is necessary for efficient silica removal. In the sludge blanket type precipitator, slow upward filtration through the suspended sludge blanket permits prolonged, intimate contact of the water with an excess of the magnesia-containing sludge. pH also has an effect on the removal of silica. The percent silica removed increases with increasing pH until the pH reaches approximately 10.1. Further increase in pH decreases the percent silica removed. The greater the percentage of silica removed at a lower pH, the less important is the control of pH. Retention time also has an effect on silica removal. For example, water at 73°F had 40% of its silica removed after 1 hr and 57% of its silica removed after 3 hr.

Temperature also has an effect on silica removal. Higher temperature operation also reduced the required residence time. Because of this significant effect of temperature, hot lime–soda softening is much more efficient than cold lime–soda softening in removing silica by the magnesia process. However, heating of water for pretreatment is relatively expensive. The water must finally be recooled to about 80–90°F before passage through contemporary RO membranes.

Macroreticular resins (particularly Rohm and Haas IRA 938 traps) pretreatment with ultrafilters and in-line coag-



ulation also offer promise of dealing with colloidal silica in practical systems. In some cases, it may be important to remove traces of heavy metals via pretreatment from a RO system. Precipitation as hydroxides or sulfides, followed by coagulation/flocculation is probably the treatment of choice here. Certain metallic ions, for example, chromate and ferrous ion, if present, may require preoxidation or reduction to easily precipitable forms in this treatment regimen.

Several other aspects of pretreatment remain to be mentioned. These include: adjustment of pH even where $CaCO_3$ precipitation is not a problem; the need to pretreat via a heat exchanger to ensure that the temperature of the influent water is compatible with membrane properties and limitations. It must also be kept in mind that some waters, particularly waste streams and surface waters, are subject to enormous variations in impurity level often from day to day or seasonally. For this reason, the more flexible methods of pretreatment, such as sludge blanket precipitation, have decided advantages.

Judging the effectiveness

A method of measuring the effectiveness of a chemical pretreatment step, particularly one designed to remove colloids and particulate or precipitable matter, is to continuously run the effluent from the pretreatment through a membrane filter under a constant pressure head, and measure the falloff in water permeation rate with time. This information can be used to calculate plugging factors for the pretreatment effluent which are held by some to have predictive value. For example, a plugging factor of, say 10%, indicates that RO membranes can operate on the feed from this pretreatment almost indefinitely without serious trouble, whereas a plugging factor of 90% indicates that the pretreatment is inadequate in that its effluent will plug the RO membrane very rapidly. In either case, cleaning can usually restore the membrane to its original effectiveness. This technique of measuring pretreatment effectiveness has been stated to be reliable for some membranes (Du Pont's B-9 permeator) and not as reliable for others (spiral wound cellulose acetate).

The efficiency of coagulation/precipitation reactions in general can, to some extent, be monitored by "jar" tests, but effective applications of the technique to RO pretreatment have not been established. An ultrasensitive photoelectric photometer, reading accurately to 0.01 JTU may have predictive value with regard to colloid removal by pretreatment, but no reports of applications of this technique to RO pretreatment have appeared. At the present time, predictive estimation of pretreatment methods for RO is most safely obtained by the continuous use, over a long period of time, of a small pilot plant replicate of the proposed full-scale RO system at the same installation site or at least with an identical feed.

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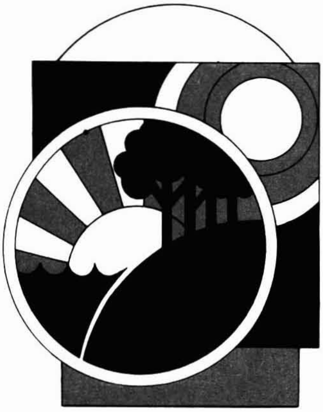

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FEATURE

Organic chemical industry's waste waters

Treatment technology is showing good progress despite a slow start in the environmental age

Paul S. Minor
Consulting Chemical Engineer, Reston, Va. 22091

The organic chemical industry is complex. There are thousands of companies involved in the manufacturing chain which starts with basic raw materials such as petroleum, coal, natural gas, and brine and leads to the almost endless consumer and engineering products associated with twentieth century life. The technology to accomplish this conversion has evolved in the last 60 years. The U.S. organic chemical industry, which now leads the world in production, was virtually nonexistent at the beginning of World War I, when Germany had a monopoly on organic chemical manufacturing technology.

Although pollution control technology has lagged manufacturing technology in all industries, a comparison of the complex manufacturing technology of the organic chemical industry with the status of the pollution control technology for the industry shows that this industry had perhaps the greatest gap of all at the beginning of the era of environmental concern in the late sixties. At that time, many of the major chemical corporations began to apply their exceptional technical resources toward resolving the pollution problems associated with the manufacture of organic chemicals. The effort is now showing progress as new pollution control facilities begin to go on-stream. Although a tremendous amount of work remains to be done before a complete solution to the wastestreams from this industry will be available, the last few years have shown very good progress.

As would be expected from the number of products and processes used in the organic chemical industry, the wastewater has widely varying characteristics. In dealing with wastes from this industry, the pollution control engineer can generally expect to face most of the following properties:

- high concentrations of COD—consisting of an array of organic compounds with widely varying biological degradability and adsorption characteristics
- high total dissolved solids
- high COD/BOD ratio
- possibility of small amounts of compounds inhibitory to biological treatment
- possibility of radical variations in waste characteristics as product mix changes
- possibility of spills or emergency conditions which can stress or destroy a treatment system through toxicity or corrosion
- possibility of heavy metals from the catalysts used.

All of these properties act to make the chemical industry's waste treatment more difficult than treating municipal wastes. Although some organic chemicals can be manufactured without producing wastes with any of these characteristics, the bulk of the organic chemical manufacturers must face these properties in designing a treatment system.

Organic chemical plants do have many sources of wastes in common with other industries, such as wastes from barometric condensers, product washwater, equipment cleanup, and leaks. In addition, the chemical industry is unique in that water is produced by many of the chemical reactions. This water, since it is formed in contact with reactants and products, is usually heavily contaminated, and is inherent in producing the product. Water used as a medium for chemical reactions is similarly contaminated, yet can only be reused to a limited degree in many cases because of the adverse effects impurities will have on the chemical reactions.

In addition to the waterborne wastes, most organic chemical plants engaged in making purified products will have one or several distillation column bottom streams which present a disposal problem. This stream represents the concentrated impurities that have been separated from the purified product. In certain manufacturing processes, some of these streams can be recycled to the reactors where they are converted into useful products, but it is almost certain that somewhere in an organic chemical plant, a concentrated stream of "heavy" or large-molecular-weight impurities will be produced. These streams are usually viscous and contain a wide range of compounds. Since nonvolatile impurities from the entire manufacturing plant are concentrated in this stream, it can contain many toxic compounds, including heavy metals. This stream is a serious disposal problem. Land disposal can be hazardous.

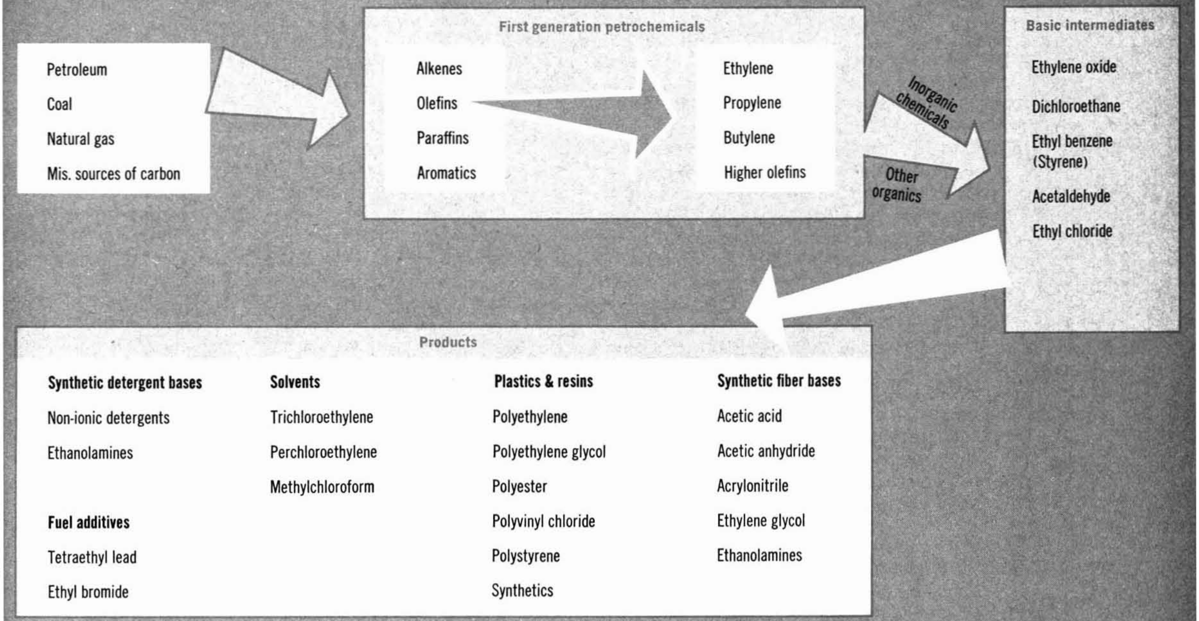
Incineration (*1*) at high temperatures is the common method for disposal of this stream. The liquid composition is usually set such that the stream is pumpable to the incinerator. If the stream contains chlorinated compounds, the incinerator will produce hydrogen chloride as well as carbon dioxide and water. The incinerator off-gas must then be scrubbed. It is sometimes possible to recover a hydrochloric acid solution sufficiently pure for some in-plant use. Otherwise the purge from the scrubber becomes a waste stream.

Reuse of water and waste chemicals

Because of the difficulties in treating wastes with the characteristics just described, treatment is, in effect, a last resort. It is used only after in-plant controls, water reuse, and chemical recovery have been applied to the economic limit. A good in-plant control program will minimize treatment needs by decreasing the contact of fresh water with the process streams, preventing pump seal or piping leaks from entering the waste stream, and allowing for the handling of spills with a minimum of flushing to the waste treatment system. Most organic chemical companies that have entered into programs at improving their in-plant practices have been pleasantly surprised at the waste reductions possible.

Waste reuse (*2*) is one technique which organic chemical companies are beginning to apply. The major attraction for the reuse of wastewater is that the quality of the water reused can be set by the manufacturer himself, based upon the requirements of his process, rather than

Some products derived from organic chemicals



Source: P. S. Minor

by a regulatory agency. If the goal of zero discharge of pollutants is to be even approached, it will be by the use of extensive water reuse. Complications occur with chemical plant wastes high in dissolved solids. These solids limit the number of reuse cycles obtainable before process problems associated with the buildup of impurities in the water begin to appear. Methods for removing the critical impurities from the recirculating stream must be applied.

To enhance water reuse, precipitation, evaporation, ion exchange, electrodialysis, and reverse osmosis are techniques which have the theoretical capability of isolating specific troublesome contaminants from the water stream. The implementation of these technologies, economically, in commercially operating plants has been a slow process requiring a case-by-case analysis. In addition, any method of separation that produces a mixed concentrated stream of pollutants must be accompanied by either an in-plant use or an end-disposal scheme, if any environmental progress is to be realized for the relatively high cost of the concentration step. The economic removal of accumulating impurities and the finding of uses for these impurities are essential if water reuse is to become widespread in the organic chemical industry. There are, presently, a few specific examples where waste streams from organic chemical plants have been treated to remove the specific contaminants and the stream has been reused in the chemical process.

In a project partially funded through an EPA demonstration grant, Dow Chemical is now using a 18% brine waste stream from its phenol plant (Midland, Mich.) as a feed brine for its chlorine plant. Pilot electrolysis tests showed that the brine could be used in the chlorine plant if the phenolic and carboxylic acid compounds were removed. The phenolic compounds (largely phenol) are adsorbed on activated carbon. The brine pH is then lowered and the carboxylic compounds (mainly acetic acid) are reacted with chlorine in a photochemical reaction. Methyl chloride is then stripped from the brine and either used or burned to recover the chloride value. The brine stream thus treated is then suitable (after saturation) for use as a feed to the chlorine/caustic plant. The phenols are removed from the activated carbon by a 4% caustic solution which is recycled to the phenol plant. This system therefore uses both the water and the impurities which had previously prevented the reuse of the water.

Certain wastewaters can be recycled to cooling towers to replace the fresh water used as cooling tower makeup. This practice can be attractive for using water contaminated with organics, but relatively low in dissolved salts, such as evaporator condensates or drying still overheads. Biological activity in the circulating cooling water will reduce the organics in the water. Sun Oil Co. has reported extensive reduction in phenols by this method over several years operation. Care must be taken to distinguish between the biochemical degradation of organic wastes in cooling tower systems and the less environmentally sound practice of using the cooling tower to strip volatile organics from the water into the air.

Another common practice has been product integration for reduction of pollution loads. This practice is part of the technique of chemical recovery. Products are removed from the waste stream for reuse in the plant which formed them, by using the recovered chemicals at a different plant on the same site, or by shipping the waste stream to another plant which has a use for the major components. This practice is well developed in the organic chemical industry, largely for economic reasons. It is common for one manufacturer to establish a plant near another manufacturing facility to take advantage of its by-products. Without this practice, pollution loads from the organic chemical industry would be many times their present value. Also fortunate from an environmental viewpoint is the fact that many processes, which produce by-products for which no use could be found, have been forced out of the market.

An example of recovering waste chemicals for reuse in the same plant which generated them is the activated carbon application by Monsanto (Anniston, Ala.), in which the nitrophenol and the *p*-chlorobenzene are recovered and returned to the process. One outstanding example of good product mix selection is the PPG Industries' chlorocarbon complex (Lake Charles, La.) where several of the plants manufacturing highly chlorinated compounds can use, as their feedstock, "wastes" from the vinyl chloride or ethylene dichloride processes at the same site.

Examples of shipping wastes from one plant to another can be found in the petroleum and paper industries where the wastes have been used as the base for a profitable line of resins by many companies. Merichem (Houston, Tex.) has rebuilt a business on the utilization of the waste caustic from gasoline sweetening, recovering sodium sulfide for sale to the paper industry and cresylic acid for sale to other chemical companies. With the present environmental ethic, all of these practices should increase radically in the next few years, thereby increasing the efficiency of the industry in most cases.

Pretreatment

Pretreatment is especially important in treating organic chemical plant wastes. Equalization, mixing, pH adjustment, flocculation/coagulation, primary settling, flotation, and oil separation are all commonly used to prepare the wastewater for either biological treatment or carbon adsorption. Troublesome to many organic chemical companies are those streams which have concentrations on the borderline between levels normally associated with recovery in the process plant and levels usually associated with waste treatment. Streams with soluble organics concentration between 0.5–5 wt % (5000–50,000 ppm) usually fall in this category.

In this gray area, although conventional chemical engineering techniques such as stripping, extraction, evaporation, or distillation can usually further reduce the concentration in the aqueous stream, the size and energy requirements of the expensive stripping or distillation columns begin to rise exponentially. Incineration at this level of concentration is usually not feasible because of high fuel requirements.

Evaporation is the most developed technique for concentrating waste streams containing mostly compounds of negligible vapor pressure. Evaporation modifies concentrations out of the awkward range into a higher quality water suitable for biological treatment or reuse, and a concentrated stream suitable for chemical recovery or incineration. Fouling tendencies characteristic of most wastewaters often present problems. Comments made earlier on removal of impurities from waste streams to allow reuse of water apply here also. A case-by-case stepwise development is required, with special attention given to achieving an acceptable fouling rate. Evaporation will be the most widely used technique in the next few years.

Distillation or stripping, used to separate the single waste streams of intermediate concentration into a relatively dilute stream and more concentrated stream, is applicable for compounds with appreciable vapor pressure. These techniques are more expensive than evaporation. In all cases, the resulting concentrated stream must be either used in some manner in the plant or incinerated.

Membrane separation processes theoretically could reduce the costs associated with modifying the concentration of streams of awkward concentration since they theoretically require less energy and are compact. There has been very little success in this area to date, however, because of the difficulty of maintaining membrane efficiency in the harsh environment of the organic chemical waste streams. Perhaps recent improvements in membranes will eventually allow more use of this technique.

Extraction, in which the waste stream is contacted with a liquid with a more favorable solubility for the contaminant, is a well-developed chemical processing technique. It has not been widely applied to waste streams to date because of the need for distillation to separate the solvent from the extracted contaminant, and the lack of inexpensive solvents which have a water solubility sufficiently low to prevent excessive losses in the water stream and additional environmental pollution.

Anaerobic biological treatment has been proved to be an effective means of pretreatment for many organic chemical wastes. Anaerobic systems can be acclimated to accept wastes which cannot be handled in aerobic systems and convert them to an acceptable feed for activated sludge or aerated lagoon systems. Such a system alone cannot produce a satisfactory effluent. Industrial experience includes Union Carbide's petrochemical complex in Texas City (Tex.).

Trickling filters are sometimes used as pretreatment for organic chemical wastes. With sufficient recycle of the trickling filter effluent, a certain amount of protection against strong chemical wastes is provided. Rollins Purle, for example, is a waste disposal contractor who uses this method. The successful application, with perhaps the widest variation of wastes faced by any company, speaks well for the trickling filter performance in some organic chemical wastes.

Biological treatment

Through proper acclimation and care in operation of both the chemical plant and the waste treatment plant, a large percentage of organic chemical wastes can be biologically treated. Great care must be taken, however, to level out waste characteristics. For those wastes which cannot be treated by biological systems, activated carbon is a useful alternative.

In designing a waste treatment system for organic chemical wastes, many of the precepts and methods for design of sanitary waste systems are no longer valid. A much more fundamental understanding of the nature of the waste and its variation is required. Piloting is necessary almost without exception. The use of BOD_5 as a primary parameter of study is usually not satisfactory. COD, TOC, and extensive analyses for specific chemical components are needed. This effort is leading to a more basic understanding of biological systems.

Since it is expensive to design a biological or activated carbon system capable of handling the waste concentration extremes which occur in the average organic chemical plant, changes in plant operating philosophy to accomodate the waste treatment plant would save considerable investment. The implementation is difficult and most waste treatment systems in organic chemical plants still face these swings. A large portion of the waste treatment systems not operating well can be attributed to larger swings than expected, in both waste characteristics and flows from the production plant.

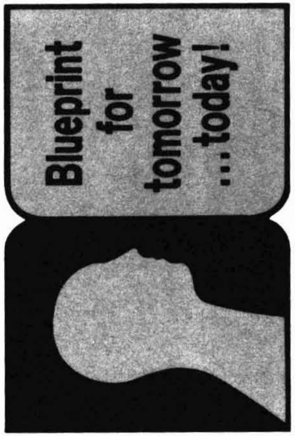


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TABLE 1

Full-scale activated carbon systems treating organic chemical wastes

Company	Granular systems	Wastewater flow, gpd	Contaminants removed	Reactivation scheme	Comments
Allied Chemical Birmingham, Ala.	Hydrodarco 4000	3,000	Phenols	None	.....
Dow Chemical Midland, Mich.	Witco 718	145,000	Phenols	4% NaOH	Removes phenols from 18% brine solution for use in chlor/alkali plant. Reactivation solution recycled to phenol plant
East Coast Manufacturer N.J.	Filtrasorb 400	58,000	Polyethers	Thermal	Discharges to municipal system
General Electric Pittsfield, Me.	Filtrasorb 300	Batch treatment (varies with use)	Color	Thermal	Used for treating a variety of waste stream in-plant. On-stream December 1971
General Electric Selkirk, N.Y.	Filtrasorb 300	300,000	Phenolics Toluene Color	Thermal	.....
Hardwicke Chemicals Elgin, S.C.	Filtrasorb	20,000	Mixed organics	Thermal	Subscribes to Calgon Adsorption Service
Hercules Chemicals Hattiesburg, Miss.	Filtrasorb 400	3,200,000	COD Mixed organics Wood sugars	Thermal	Just completing start-up
Monsanto Anniston, Ala.	Filtrasorb 300	65,000	*p*-nitrophenol *p*-chlorobenzene	Chemical	Reactivation chemical with recovered product returned to process
Rhodia, Inc. Portland, Ore.	Filtrasorb 400	150,000	Chlorophenols	Thermal	.....
Schenectady Chemicals Schenectady, N.Y.	Filtrasorb 300	22,000	Phenols Resorcinol Xylol	Thermal	On stream March 1973
Stephan Chemical Co. Fieldsboro, N.J.	Filtrasorb 300	15,000	Mixed organics associated with liquid detergent intermediates	Thermal	On-stream June 1972
Stauffer Chemicals Skaneateles Falls, N.Y.	Filtrasorb 300	8,000	COD from washout of batch equipment used to make mixed detergents and wash compounds	Expended carbon saved and shipped to central processing facility where a tank car load is accumulated	Treats segregated waste side-stream. Effluent then joins main waste stream
Reichhold Chemicals Tuscaloosa, Ala.	Filtrasorb 300	500,000	Phenols, BOD, COD	Thermal	Treats concentrated waste resulting from extensive in-plant water use reduction. On-stream late 1972
Sherwin-Williams Chicago, Ill.	Nuchar WV-G, 12 × 40	65,000	*p*-cresol	10% NaOH	.....
Vicksburg Chemical Vicksburg, Miss.	Hydrodarco 4000	10,000	Phenols	NaOH	.....
Ashland Chemicals Great Meadows, N.J.	Hydrodarco[a]	140,000	Color, COD	None	Biological treatment with 85 ppm of carbon added to influent
Dow Chemical Midland, Mich.	Nuchar[a]	14,000,000	Mixed organics	None	Biological treatment with carbon added to influent
Koppers Chemical Follunsbee, W.Va.	Nuchar[a]	20,000	Phenolics	None	Used when biological treatment efficiency drops

[a] Powdered system.
Source: P.S. Minor

Activated sludge systems, aerated lagoons, and oxidation ponds make up the vast majority of biological treatment systems in the organic chemical industry. To minimize the effects of changes in waste characteristics, completely mixed systems have been favored over plug flow systems. It has also been necessary to use high retention times, normally a minimum of 24 hr. This retention time is required because:

- Influent concentrations are high.
- Increased protection against swings in waste characteristics is needed.
- Biological activity is slow.
- Kinetics of the completely mixed system are not as favorable as the plug flow system.

Start-up times for biological systems handling organic chemical wastes are longer than for systems handling sanitary wastes, because of the required acclimation period. A system is commonly started on innocuous wastes which are gradually displaced with the plant wastes. Because of the extremely unfavorable kinetics of taking a reaction at fairly high concentrations to completion in a single completely mixed step, staging is a common practice in organic chemical waste treatment systems. Thus an aerated lagoon preceding a completely mixed activated sludge system is commonly employed.

Reaching an optimum economic sequence requires the balancing of many factors, based upon a thorough knowledge of the waste characteristics. The extension of chemical reaction optimization techniques, used in designing chemical process reaction systems to the waste treatment plant, is relatively new and is a contribution to treatment technology which the organic chemical industry is in a unique position to make.

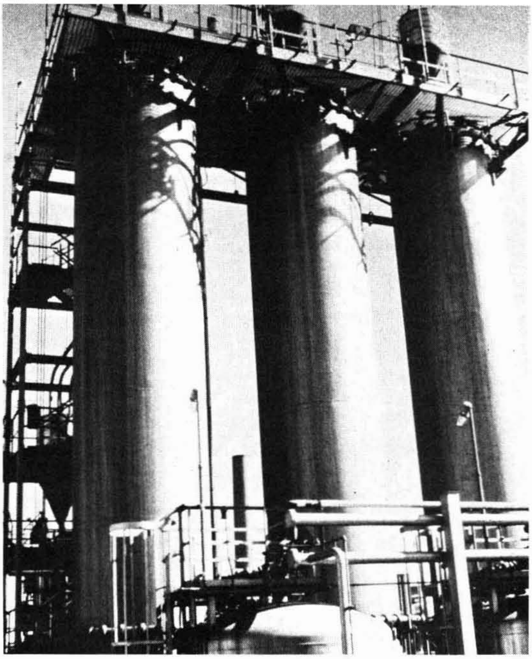
As an example of the different sequences which can be used because of varying waste characteristics, Union Carbide is utilizing an anaerobic-aerated stabilization basin–faculative oxidation pond sequence at its Texas City complex, an aerated stabilization basin-pure oxygen activated sludge sequence at Taft (La.), and a straight oxygen-aerated activated sludge system at Sistersville (West Va.). The use of pure oxygen might be advantageous in certain organic chemical wastes. The claimed increased stability and flexibility of pure oxygen systems should be beneficial. In addition, oxygen is commonly used in many organic chemical processes. Pure oxygen is currently being used on a full-scale system at an American Cyanamid pharmaceuticals plant where the wastewater has some of the properties of organic chemical plant wastes.

The rotating biological disk would appear to have some value in organic chemical waste treatment, at least as a pretreatment technique because of the relative ease in which it can be arranged in a series of stages. To the author's knowledge, however, there is no full-scale biological disk system now operating on organic chemical wastes in the U.S. Du Pont is expected to have the first full-scale operation in its Chattanooga (Tenn.) nylon plant where it will be used basically for nitrification on a low COD waste.

Physical-chemical treatment

The properties of many organic chemicals complicate biological treatment. Activated carbon can be an attractive alternative. It offers the following advantages over biological systems for many wastes:

- less sensitivity to temperatures
- less time required for start-up
- higher removal of COD for many (but not all) wastes
- insensitivity to toxics (and will in fact remove most toxic organics)
- effectiveness in streams with high dissolved solids.


Carbon adsorption. *BP Oil's refinery meets first-stage ultimate oxygen demand standards set by the Delaware River Basin Commission*

Since it can be regenerated and is easily prevented from entrainment into the wastewater by screens, granular carbon has been chosen over powdered carbon in the majority of applications. The technology for evaluating the applicability of granular activated carbon and the ability to design commercial systems from pilot data are well established.

A major inhibition to the widespread use of granular activated carbon has been the high capital cost of installing thermal regeneration facilities in small installations. Calgon took a significant marketing step when it introduced the Adsorption Service concept in 1972 (*ES&T*, Jan. 1974, p 14). By using this service, customers can lease carbon adsorption systems at a guaranteed monthly charge. The company assumes the responsibility for regeneration at central facilities.

For the organic chemical industry, methods of regeneration other than thermal can often be attractive. The very high COD levels, faced by activated carbon systems in organic wastes, demand high regeneration rates. At the usual thermal regeneration loss of 5% per cycle, this can lead to high carbon makeup requirements. Chemical regeneration can save much of the investment and carbon loss associated with chemical regeneration. If a use for the regenerating chemical solution can be found, this is usually an attractive route.

Powdered activated carbon has a lower first cost and a higher adsorption rate than granular carbon. Since there has been no commercially available regeneration technique for powdered carbon, its use in the organic chemical industry has been limited. Westvaco has been buying back spent powdered carbon from corn syrup decolorization applications and regenerating it in a prototype thermal regeneration system in Covington (Va.). The commercialization of an economic reactivation system for powdered carbon is a major requirement for the wide use of powdered carbon as a complete waste treatment step.

Powdered carbon is beginning to play an important role in combined carbon–biological systems. Because of the ability of activated carbon to give good performance in areas where biological systems are weak and the equivalent ability of biological systems to improve on activated carbon results, a combination of the two systems offers the promise of enhanced performance. This concept is now undergoing extensive testing, using powdered carbon material in activated sludge systems.

The carbon is metered into the system with the influent at a concentration normally less than 100 g/ml. It is recirculated and purged along with the biological solids at a rate which maintains an equilibrium concentration of 1000–2000 mg/l. The powdered carbon increases sludge settling, reduces the foaming tendency, and smooths out the performance of the biological system by adsorbing soluble components at their higher concentrations and later desorbing them when the concentration decreases. Du Pont has extensively piloted this concept and is a pioneer in this area. It has announced a full-scale system to be in operation by 1975.

Granular activated carbon finds application in removing aromatic, branched or halogen-containing, or other complex organic molecules of limited solubility in water. These are the areas where biological systems are weakest. For many highly soluble organic chemicals such as short chain alcohols, biological systems are more effective. Since only carbon can remove certain components of organic wastes while only biological systems are effective in other areas, mixed wastes of these compounds can be very difficult to adequately, treat by either system alone. The use of biological systems combined with granular activated carbon systems is still relatively rare in the organic chemical industry, however.

The selection of the best position to place the activated carbon column in relation to the biological system is not always an easy decision. If the carbon columns are installed ahead of the biological system, they will protect it against toxics and smooth out concentration swings which have been such a serious operating problem in many plants. The carbon columns will face a very high COD concentration. If the columns are placed after the biological system, less carbon is required since the carbon sees a waste much lower in COD. The biological system is more susceptible to upsets, and a failure can overload the carbon columns with a resulting poor effluent quality. The final decision obviously depends to a large degree upon a detailed knowledge of the wastes the entire treatment system will face in actual operation.

Regulatory status

The organic chemical industry has been extremely difficult to categorize sufficiently for the development of national effluent guidelines as is required under P.L. 92-500. The EPA contractor for developing effluent guidelines for the organic chemical industry suggested that it be divided into four categories for this purpose:

- nonaqueous processes
- processes in which water is used only as diluent stream, for quenching, or as an absorbent
- processes using only liquid phase reactions
- processes using batch and semicontinuous processes.

Suggested allowable pollutants per ton of product were then suggested for each of the above categories based upon the contractors judgment of best practical technology—staged biological treatment and/or carbon adsorption.

Although this novel approach simplifies a very complex situation, the differences in waste properties between plants which fall within the same category are so great as to severely limit the usefulness of any basic guidelines along these categories. Major waste characteristics are set by the chemical composition of feedstocks, intermediates and products, as well as the physical nature of the process. While the type of physical process used in manufacturing may affect the waste flows and concentrations, it is the chemical nature of the waste which dictates the type of treatment possible.

The Union Carbide Corp. (3), after an extensive discussion on the variations between wastes in the organic chemical industry, presented an alternate approach to the Effluent Standards and Water Quality Information Advisory Committee (*ES&T,* Dec. 1973, p 1093) in which they suggested:

- Biological treatment met the definition of Best Practical Control Technology Currently Available.
- An empirical "treatability" equation should be used to adjust a base warm weather soluble BOD value obtained by biological treatment at a feed concentration of 100 mg/l. for differences in concentration, temperature, and suspended solids.

One missing part in this otherwise fine proposal is failure to include activated carbon treatment as a step in some cases. There are some organic chemical wastes which can be treated adequately only by including activated carbon in the treatment sequence. A major point to be resolved is just how much compensation a manufacturer should be allowed in biological treatment of his wastes before activated carbon treatment or a mixed system is required. This approach leads to consideration of the economic impact which will be imposed on the chemical industry.

It must be realized that whatever the form of the final guidelines, a large portion of the manufacturers will have plants which for various reasons will fall outside the "standard," and that much of the regulation of the organic chemical industry will be by a detailed case-by-case basis. While this is undesirable from a regulatory viewpoint in that it will require many engineers familiar with the industry to work out stringent yet fair effluent allowances, it appears that in this complex industry there is no other way.

Additional reading

(1) Santoleri, J. J., "Chlorinated Hydrocarbon Waste Disposal and Recovery Systems," *Chem. Eng. Prog.*, **69,** 1 (1973).

(2) "Complete Water Reuse: Industries' Opportunity," Collection of Papers, AIChE-EPA Technology Transfer Conference, Washington, D.C., April 23–27, 1973.

(3) Conway, R. A., et al., "Treatability of Wastewater from Organic Chemical and Plastics Manufacturing—Experiences and Concepts." Report by the Research and Development Dept., Plastics and Chemicals Div., Union Carbide Corp.

Paul S. Minor *is a consulting chemical engineer, specializing in industrial pollution control. He was formerly head of EPA's industrial technology transfer program. His industrial experiences include organic chemical process development and start-up activities at Union Carbide, PPG Industries, and Parkson Corp.*

Coordinated by LCG

INDUSTRY TRENDS

The Carter Oil Co. (Houston, Tex.) and the Columbia Coal Gasification Corp. (Wilmington, Del.) have signed agreements providing for the development of certain low-sulfur coal reserves in West Virginia, and a future gasification opportunity for certain coal reserves in Illinois.

International Paper Co. (New York City) authorized plans for major expansion of the company's Androscoggin pulp and paper mill (Jay, Me.), contingent on acquiring necessary environmental permits, availability of needed transport, and resolution of current local tax issues.

Henningson, Durham & Richardson, Inc. of Texas (Dallas, Tex.) has designed the first plant in the U.S. to use pure oxygen for wastewater treatment. The plant, at Lewisville, Tex., will surpass the tight Texas Water Quality Board and EPA standards.

Magnetic Engineering Associates, Inc. (Cambridge, Mass.) is now Sala Magnetics, Inc., after acquisition by Sala International AB of Sweden. Sala Magnetics will continue commercial development of high-gradient magnetic separators.

Fluor Corp. received a favorable tax ruling on the acquisition of Pioneer Service & Engineering Co. (Chicago). Pioneer was one of the first engineering firms involved in nuclear power plant development. The acquisition should proceed promptly.

Analytical Instrument Development, Inc. has recently moved to a new location at Avondale, Pa. The company manufactures environmental instrumentation used to analyze industrial environment contaminants and air pollutants.

The Midwest Research Institute announced that Fiscal 1973 produced the institute's largest research volume in its 29-year history—$7.6 million—a 13% increase over 1972.

Americal Air Filter Co., Inc., has been selected to supply $11.7 million worth of air pollution control equipment for TVA's steam generating plant at Kingston, Tenn.

Poly Con Corp. has signed a manufacturing and sales agreement with Duro Dakovic (Slavonski Brod, Yugoslavia). This entitles Duro Dakovic to make and sell Poly Con products in Eastern Europe, Syria, Libya, and Egypt.

Browning-Ferris Industries, Inc. announced revenues of $146,297,000 for the six-month period ended March 31, 1974—the highest first half revenues in the company's history.

Systems Control, Inc., a company in the fields of electric power, environmental control, and defense and aerospace, and other services, has relocated to a new three-building complex at Stanford Industrial Park, Palo Alto, Calif.

Alpha Analytical Laboratories of Alpha Metals, Inc. has been appointed U.S. distributor for the line of colorimetric chemical analysis equipment made by Tintometer, Ltd. (Salisbury, England).

Dow Chemical U.S.A. is to supply 49 million board feet of Styrofoam brand plastic foam to Alyeska Pipeline Co. to aid in building the Alaska pipeline. The $7 million order, to date, was the largest of its kind Dow ever received.

The Heil Co. will supply a 15 tph complete waste-shredding system to Chaffee County, Colo. The plant will be located near Salida, the county seat. Shredded waste will be disposed of at a nearby landfill site.

Du Pont has made a joint agreement with the Diamond Shamrock Corp. (Cleveland, Ohio) to demonstrate the application of improved "Nafion" perfluorosulfonic acid membranes in electrolytic processes for chlorine and caustic manufacture.

Hercules Inc. is constructing an agricultural chemicals plant adjacent to its methanol facility at Plaquemine, La. The plant will produce Hercules' "Torak" miticide-insecticide.

Digital Acoustics, Inc. (Santa Ana, Calif.) announced delivery of the first of 17 portable community noise monitoring systems under a contract with the U.S. Department of Housing and Urban Development.

CPL Corp. (East Providence, R.I.) has acquired the New England Chemical Supply Div. of Nyanza, Inc. (Lawrence, Mass.), a maker of aqua ammonia, and processor of chlorine and sodium hypochlorite used in water and effluent treatment.

Zurn Industries, Inc. ascribed its record earnings (fiscal year ended March 31, 1974) to record sales, sale of its heavy construction div., and a way to dispose of its waterfront development project. Income was $1.37/common share, up 26¢ over that of the previous year.

Ethyl Corp. (Richmond, Va.) announced the completion of a significant gas discovery in Matagorda County, Tex.

El Paso Environmental Systems Inc. (El Paso, Tex.) says that pilot studies and EPA-funded plants demonstrated that spiral wound reverse osmosis (RO) membranes apply to municipal wastewater treatment.

REECO (Regenerative Environmental Equipment Co., Inc., Palisades Park, N.J.) will install REECO "Re-therm" fume and odor control system at the Lancaster, Pa., facility of Armstrong Cork Co.

Procon, Inc., a Universal Oil Products Co. subsidiary, will help to build a $250 million grassroots oil refinery, Europe's largest, at Sines, Portugal, for Petrosul (Portugal).

The Singer Co. logged sales of metering, controls, and water resources equipment at $191.9 million in 1973, as compared to $198.9 million in 1972.

Ecodyne Corp will build a 185,000-gpm mechanical draft, closed-cycle cooling tower for the Georgia Power Co.

The Torit Corp. will be merged with Donaldson Co., Inc. Terms involved an exchange of stock.

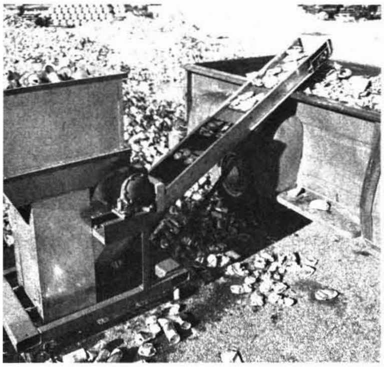
American Air Filter Co. plans to acquire all outstanding shares of Industrifilter AB of Sweden, if the Swedish Riksbank (national bank) approves.

Northeast Utilities (Hartford, Conn.) has tendered documentation to the U.S. Atomic Energy Commission in support of its plan to build a two-unit, 2300-MW nuclear generating station at Montague, Mass.

Kaiser Engineers, Inc. (Oakland, Calif.) will assist in management of construction activities of Cleveland Electric Illuminating Co.'s Perry Nuclear Power Plant to be built at North Perry, Ohio.

Alyeska Pipeline Service Co. (Bellevue, Wash.) authorized Fluor Alaska, Inc. to proceed, as general and management contractor, with construction of a marine tanker terminal at Valdez, Alaska, and pumping station for the Alaska pipeline. The work will cost $1 billion.

NEW PRODUCTS



Recovery system
Resource recovery system flattens aluminum and steel cans, and crushes glass containers as well. The machine is a self-contained portable unit, and can be equipped with a magnetic pully for separation of steel and aluminum. It is compatible with commonly used storage facilities and does not require any special support equipment. Drew-it Corp. **101**

Exhaust monitor
Portable monitor is designed especially for measuring NO in stack and exhaust emissions. It is based on the chemiluminescent reaction of NO and ozone. It is strikingly sensitive for a small size instrument. Specific to NO, the model is unaffected by SO_2, water, CO_2, oxygen, and HC_x present in normal stack gases. Thermo Electron Corp. **102**

Brush chipper
Devices are engineered for high-speed production and are available in 12- and 16-in. models. These chippers feature forged steel rotors, which allow blades to be positioned at precise angles for smooth slicing action. Also featured are two directional bed plates, turbine-type blowers, new machined steel flywheels, V-8 power, and hydraulic safety brakes. FMC Corp. **103**

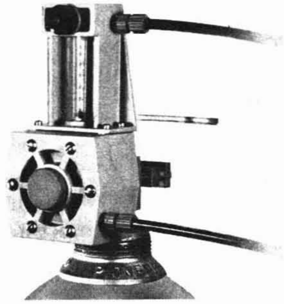
Dust collector
Small bag collector for mounting at the top of lime plant load-out stands prevents pollution and collects material previously lost. The intake hose from the collector is placed in the vent hatch and both hatches are covered with tarpaulins to help seal off the hoses. When the load-out is complete, device is shaken down and dust is returned by the intake hose to the truck. Johnson-March Corp. **104**

Opacity monitor
New opacity monitor converts to multiple stack gas instrument. It allows users to measure opacity initially and then convert to monitor up to four gases—NO, SO_2, CO, CO_2—plus opacity with the same instrument. It will monitor continuously and provide readouts in percent opacity. Model operates on a split-beam principle with a unique single detector. Environmental Data Corp. **105**

Machine mounts
Series of heavy-duty machine mounts reduce shock, vibrations, and noise levels, as well as simplify move-ins, leveling, and later relocations of production machinery. These mounts meet OSHA anchoring requirements. Plant noises are lowered with the use of a heavy rubber base, which reduces vibrations from impact and other machinery up to 90%. Sunnex, Inc. **106**

Sewer flowmeter
Sewer conduit flowmeter is ideal for a variety of wastewater flow measurement uses. It is designed to create full pipe flow in the sewer conduit, thus making the area of flow constant. It is ideal for user charge programs, infiltration/inflow field surveys, system analysis and design, enforcement actions, and plant monitoring. Portac **107**

Ultracompact delumper
Ultracompact, low headroom delumper crusher can be used in very tight spots where other more cumbersome crushers cannot fit. The unit can be placed in existing systems of ducts, chutes, or pipes. It requires only 5 in. of headroom space in-line. It handles agglomerates, lumpy solids, and homogeneous or heterogeneous materials without degrading the product. Franklin-Miller, Inc. **111**



Advanced chlorinator
Direct cylinder-mounted pressure feed gas chlorinator is designed for water and wastewater treatment. It utilizes the pressure of chlorine gas in the cylinder and requires no electrical power or water pressure to operate. It is ideal for use in remote areas and for standby emergency use. Easy to install and operate. Capital Controls Co. **112**

Chemical flocculant
Dry chemical flocculant increases the efficiency of liquid–solid separation processes in influent and effluent treatment systems. This strongly anionic high-molecular-weight polyelectrolyte is synthesized to give improved water clarification while minimizing residual sludge buildup. Useful over a wide pH range. Comes in powder form. Petrolite Corp. **108**

Sewage enzymes
Unique formulation of natural enzymes is designed for use in sewage disposal systems. The substance digests solid wastes and converts them to water and other nonpolluting end products. It contains specific enzymes for each type soil waste. It digests fats, grease, oils, proteins, starches, vegetable gums, apple and potato peels, toilet tissue, and other cellulose articles. Applied Biochemists, Inc. **109**

Air data system
Automatic air quality data acquisition system utilizes telephone lines or radio telemetry and a computerized central station. Through this system it provides real time data acquisition; the conversion, summarization, and reporting of this data; and control of the remote sensor calibration cycles. Standard features include float-battery powered remote stations and central station clock. Ball Brothers Research Corp. **110**

Reverse osmosis equipment

Reverse osmosis systems are custom designed to suit the needs of industrial customers. The process removes up to 97% of dissolved inorganic salts and virtually 100% of suspended materials from water systems. Can reduce the cost of ultrapure water production by as much as 70% in the electronics industry and for high pressure boiler feed water. El Paso Environmental Systems, Inc. **113**

Conductivity meter

Portable conductivity meter is ac/dc instrument supplied with a detachable line cord and batteries for measuring total dissolved solids. Selector switch allows the operator to select either manual or automatic temperature compensation. The unit is packaged in its own carrying case with a storage compartment in the lid. Aquatronics, Inc. **114**

Ozone calibrator

Device is designed for use with ozone analyzer or any other chemiluminescent ozone analyzer. It provides a repeatable ozone calibration source. Ozone concentrations from 5–0.5 ppm can be generated for calibration. The calibrator is stable and requires only a source of ac line voltage and external air. Analytical Instrument Development, Inc. **115**

Solid waste compactor

Compactor can compress 181 yd^3 of loose refuse per hour with a hydraulic ram force of 49,500 lb. Powered by a 10-hp electric motor and activated with pushbutton controls, the unit crushes 2.01 yd^3 of solid waste each 4-sec cycle. Compaction ratio is 5 to 1 for general refuse. Its charging box will accommodate objects up to 58½ in. wide, 48 in. long, and 30 in. high. Tubar Waste Systems **117**

Effluent monitor

Monitor measures and records concentrations of suspended solids in industrial effluents, as well as in effluents from wastewater treatment plants. It also is capable of helping to locate the sources of pollution in a plant system. It is self-cleaning. It can be installed in open streams or on existing pipelines. It eliminates the need for a sampling pump. Biopherics Inc. **121**

Trickling filters

Trickle filter media features easy handling of shock loads, easy installation, and excellent biota-oxygen contact. According to the manufacturer, the devices greatly simplify the design of new wastewater treatment systems and are ideal for upgrading existing systems. Capacity increases up to 600% are claimed possible by installing the new media in place of stone or slag. Norton Co. **122**

Anionic polymer

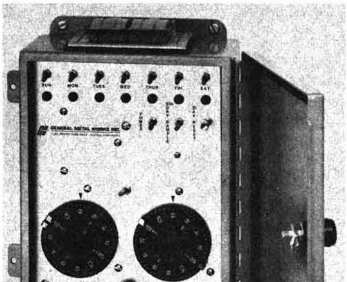
Liquid polyelectrolyte containing a high-molecular-weight anionic polymer aids liquid–solids separations, thickening, and oil emulsion treating. It increases the efficiency of clarifiers, vacuum filters, thickeners, centrifuges, and separators in both large and small systems. Supplied in 5-gal pails, and 30- or 55-gal drums, it can be used directly from containers without mixing or blending. Chemed Corp. **116**

Wastewater flow recorder

Recorder permits automatic and accurate recording of wastewater flow volumes in manholes, wet wells, and other below-grade channels. Special stainless steel mechanical linkage between recorder float and recording mechanical linkage between recorder float and recording mechanism avoids malfunctions that often are encountered when above-ground readings are required. BIF SaniTrol **118**

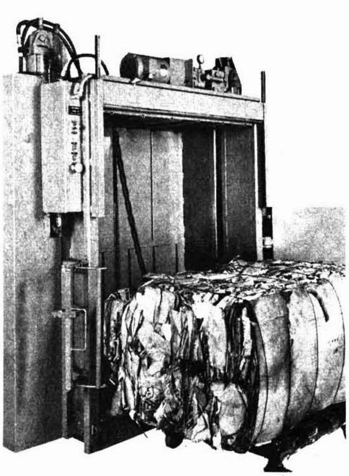
Particulates monitor

Device monitors suspended particulates in both ambient air and industrial working areas. It provides an accurate mass determination using the beta-radiation attenuation measurement technique. Suspended particulate matter is collected on a fiberglass filter tape from a preset volume of air. Its calibration is unaffected by variations in particle size distribution or chemical composition. Lear Siegler, Inc. **119**



Timer/programmers

Devices are designed to use with line of high-volume air samplers, and is applicable for use with most any timed device. One model will automatically initiate a device for a 24-hr time period every six days. When used in conjunction with a high volume air sampler, particulate matter is collected in compliance with the sixth day format in the *Federal Register*. General Metals Works, Inc. **120**



Waste paper baler

Baler compresses corrugated cartons and other paper waste into convenient bales. Forming a 29 × 60 × 42-in. bale, weighing about 700 lb, the device operates with a closed loop hydraulic system. It is powered by a 7½-hp electric motor and has spring-loaded hold-downs, front and back. Cycle time is 32 seconds. Easily movable. Uhrden, Inc. **123**

Chemical flocculant

Dry chemical flocculant reduces sludge in both influent and effluent industrial treating systems. It is a cationic electrolyte especially synthesized to work over a wide range of pH as a prime flocculant and sludge dewatering aid. The resulting sludge is higher in density and lower in total weight than that produced from inorganic salts. Petrolite Corp. **124**

Tall treatment stacks

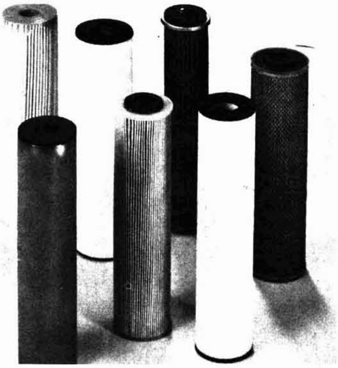
Tall stacks for corrosive service require little or no maintenance, even when exhausting highly corrosive acids and alkalies and fumes from complex chemical operations. Stacks are made in 10–25-ft sections 2–13 ft in diameter. Fabricated from a special polyester reinforced fiberglass plastic, the stacks meet specifications for strength as well as corrosive strength. Heil Process Equipment Co. **125**

Shaker filter mechanism

Eccentric-shaft shaker mechanism gives doubly efficient bag cleaning with high-performance fabric filtration of abrasive, hygroscopic, and submicron particulate. It has high-temperature capabilities. It is designed for low air velocities into the filter so that abrasive particulates, such as fly ash and some metal oxides, will not cause premature filter media wear. General Resource Corp. **126**

Water test meter

Low-cost dissolved solids, water test meter reads directly in parts per million of total dissolved solids. It is portable, weighing less than 10 oz, and features solid state circuitry and special rugged construction. Automatic temperature compensation from 55–125°F is built into the meter, with 2% meter accuracy. Devon Products, Inc. **127**



Filter media

Miscellaneous filter media is suitable for use in industrial cartridge-type filtration systems. Guide is provided to the proper selection of cleanable or replaceable filter media according to flow rate, pressure drop, temperature, viscosity, and chemical compatibility. Filter cartridges of porous stainless steel, pleated wire mesh, pleated cellulose, and wound fiber and porous polypropylene are included. Service Filtration Corp. **128**

Area CO monitors

Series of monitors are designed to provide full, continuous, and plant-wide or field station monitoring. Most are fitted with dual visual-audio alarms that alert when CO concentrations reach a predetermined danger level. The monitors have outputs for strip chart recorders to meet OSHA regulations for record-keeping. Remote central monitoring is possible. Energetics Science, Inc. **129**

Wastewater spectrophotometer

Continuous-wavelength optics and precision-polished absorption cell within new spectrophotometer permits accurate and reproducible tests for water, wastes, and industrial process fluids. Complete range from 400–700 nm enable it to be readily used with all WPCA and EPA approved standard methods. Special power cell permits remote monitoring. Delta Scientific **130**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

NEW LITERATURE

Analyzer. Catalog offers the Model 44, which is an NO–NO_x chemiluminescent analyzer. Principles of operation are described, and full specifications and capabilities are given. Thermo Electron Corp. **151**

Ceramics. Product bulletin 523, a special high-temperature selector chart describing a list of ceramic material, is available. It has been revised to list details on new materials. Aremco Products, Inc. **152**

NDT. New brochure, "Petrochemical Industry Testing & Inspection," describes nondestructive testing and inspection services for refineries, chemical plants, production fields, offshore drilling rigs, and pipelines. Peabody Testing **153**

Water level recorder. Bulletin 12 describes the Stevens Type A recorder, a float-operated device with unlimited range in water level stage. It can operate unattended for many months at remote locations. Leupold & Stevens, Inc. **154**

Reverse osmosis. A four-color brochure, describing reverse osmosis and ultrafiltration is available. It describes specific applications and provides a glossary of terms. Universal Oil Products Co. **155**

Strainers. A 16-page illustrated technical catalog, Bulletin ST-4000, describes a whole line of duplex and single-basket pipeline strainers for removing sediment, lumps, metallic particles, and other foreign matter from the fluid stream. Hayward Manufacturing Co., Inc. **156**

X-ray spectrometers. New 20-page bulletin describes a complete line of X-ray spectrometers from manually operated units to multichannel systems for process control. Siemens Corp. **157**

Submicron filtration. Bulletin PB 328, "Gelman small particle filtration systems for industry," covers new developments in the submicron filtration field. Gelman Instrument Co. **158**

Bacterial colony counter. Bulletin No. 299/7-909, "Fisher automatic bacterial colony counter," describes a new digital counter that tallies plaques, surface, and subsurface bacterial colonies in Petri dishes or membrane filters in seconds. Fisher Scientific Co. **159**

Money from recycling. A source book for those wanting to make money from recycling, "Miller's Recyclopedia" gives information on collecting and processing aluminum, glass, paper, and steel products. Miller Manufacturing Co. **160**

Gas chromatography. Book No. GCD-35, "Open tubular columns—an introduction," discusses practical operation of wall-coated and support-coated columns in gas chromatography. Perkin-Elmer Corp. **161**

Newsletter. *Rescue*, Volume 2, No. 2, a bimonthly newsletter of industrial pollution control, is available. Rollins Environmental Services, Inc. **162**

Precipitators. Study report discusses choices between a hot or cold fly ash precipitator, and how to consider such choices. Koppers Co., Inc.,/ Environmental Elements Corp. **163**

Course brochure. The course brochure explains the 1974 Environmental Law for Non-Lawyers Course, with a coupon for obtaining the text. Government Institutes, Inc. **164**

Gamma counter. Brochure describing the 1195 automatic gamma counter with "300" sample conveyor and antijam system has recently been published. Searle Analytic Inc. **165**

Water treatment system. Brochure describes patented Hussong/Couplan water treatment systems to remove heavy metal pollutants in textile dyehouse and metal processing effluents to or below EPA Effluent Limitations Schedule A, post-1977. Hussong-Walker-Davis Co. **166**

Processing equipment. New brochure describes fermenters, Funda-filters, centrifuges, Ingold electrodes, vibromixers, and other research/processing equipment. Photographs are supplied. Chemapec, Inc. **167**

Cooling water. Bulletin S600/1-0, "Cooling water cost analysis," offers engineers a handy guide for evaluating costs associated with equipment cooling systems. Baltimore Aircoil Co., Inc. **168**

Spectroscopy. Infrared bulletin #42 is a new bibliography of textbooks and monographs pertaining to infrared spectroscopy. Many topics are covered. Perkin-Elmer Corp. **169**

Ultrafiltration. An updated selection guide and catalog provides detailed information about ultrafiltration membranes and equipment for concentration, desalting, and fractionation of macromolecular solutions and suspensions. Amicon Corp. **190**

Heat recovery. Heat recovery brochure details the company's fume incineration and heat recovery equipment as the contemporary approach to cleaner air and energy conservation. Bulletin SP-177, titled, "There'll be a new dawn in the morning." Eclipse Lookout Co. **191**

Tanks. Bulletin LP-87 contains 20 illustrated case histories showing how low-cost, low-maintenance tanks and storage vessels, made with the company's polyester resin, are used in a variety of industries. ICI America Inc. **192**

Sludge removal. Catalog 33 explains unique automatic systems for removing sludge deposits from tanks, reservoirs, and process areas. Removal is enhanced by the M-7 cleaning system. Bristol Engineering Co. **193**

Underground water. Report 181 reflects the results of an intensive U.S. Geological Survey underground water study in Duval County, Tex. Texas Water Development Board, 1700 N. Congress Ave., Austin, Tex. 78701. (Write direct.)

Standards catalog. The 1974 catalog lists over 3000 international standards and more than 5600 American National Standards in 176 pages. Metric conversion, consumer affairs, and occupational safety and health are covered, along with other topics of importance. American National Standards Institute, Inc. 1430 Broadway, New York, N.Y. 10018. (Write direct.)

Fuel performance. Fuel performance map shows amount of fuel an engine consumes at a specific horsepower and speed. Maps are given for company's engines. Brochure EE-430. Allis-Chalmers **194**

Aerator system. Bulletin AE-1 describes an aerator system which has no risk of damaging a plastic liner in a waste disposal basin. There are neither moving parts nor air sprays, nor is there winter icing, or electricity. Kenics **195**

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BOOKS

Mercury in the Western Environment. Donald R. Buhler, Ed. x + 360 pages. Continuing Education Publications, Waldo Hall 100, Corvallis, Ore. 97331. 1973. $10, paper.

Proceedings based on workshop on Mercury in the Western Environment held in Portland, Ore., February 1971. Explores the effects of mercury contamination in fish and wildlife, the analysis of mercury, and the nature and occurrence of mercury-related damage to man. Book also provides status report of contemporary research on mercury pollution and toxicity.

Environment and Man. 2nd ed. Richard H. Wagner. xiii + 528 pages. W. W. Horton & Co., Inc., 500 Fifth Ave., New York, N.Y. 10036. 1974. $7.95, hard cover.

Update of the 1971 edition, this systematic study of environmental problems is for student and general reader alike. It provides a balanced treatment of such contemporary problems as air and water pollution, biocides, urban planning, population control, and the energy crises. It seeks to answer how industrial man and a clean, healthy environment can coexist.

Proceedings of Second Joint Conference on Sensing of Environmental Pollutants. 377 pages. Instrument Society of America, 400 Stanwix St., Pittsburgh, Pa. 15222. 1973. $40, hard cover.

Contains 45 papers on in-situ and remote sensing techniques of a biological, chemical, and physical nature. It focuses on sensing techniques rather than programs or platforms. These papers, first presented at the conference conducted in Washington, D.C., December 1973, cover instrument quality and measurement standardization, remote passive sensing of atmospheric pollutants, and 11 other topics.

Resource Recovery from Municipal Solid Waste: A State-of-the-Art Study. National Center for Resource Recovery. xiii + 182 pages. Lexington Books, 125 Spring Street, Lexington, Mass. 02173. 1974. $13, hard cover.

Presents an overview of the state of the art in resource recovery as it pertains to municipal solid waste. The report aims to provide the reader with background information on the subject, and serve as a reference point for further detail. It does not attempt to cover each subject or system in minute detail. It is one of a series of reports on solid waste.

Air Quality Abstracts. 773 pages. Pollution Abstracts, Inc., P.O. Box 2369, La Jolla, Calif. 92037. 1974. $75, paper.

This one-volume reference from Air Quality Abstracts summarizes and organizes significant air quality literature published since 1970. It contains nearly 6000 full abstracts covering the areas of emission sources, atmospheric interactions, air quality measurements, control methods, legal and administrative problems, and basic sciences and technologies. Air pollution effects on humans, animals, plants, and materials also are considered.

Pollution Engineering Techniques: An Overview Introduction to the Problem. 227 pages..Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1974. $10, paper.

Includes papers submitted to the 2nd Annual International Pollution Engineering Congress in Philadelphia, October 1973. The book considers virtually all principal problems encountered in pollution control, with some basic guidelines and proposals for solutions. The views are primarily those of industry and government persons. However, some academic papers are included.

Regional Growth and Water Resource Investment. W. Cris Lewis et al. xi + 172 pages. Lexington Books, 125 Spring St., Lexington, Mass. 02173. 1973. $14.50, hard cover.

Seeks to illustrate the way in which investment in water resources might influence the pace and direction of regional economic growth. The state in question is Utah, but many of the findings are generally applicable. The book attempts to broaden the stock of knowledge on this question, and thereby increase the rationality under which such investment decisions are made.

Recycling and Disposal of Solid Wastes: Industrial, Agricultural, Domestic. T. F. Yen, editor. viii + 372 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1974. $20, hard cover.

Book covers a wide range of expertise concerning the energy and biological aspects of solid wastes. Also considered are polymer-gas reactions, ionene polymers to flocculate colloids, glass and metal container recycling, protein production from cellulosic wastes, polymers for stabilizing mineral wastes, leachate formation in sanitary landfills, and animal, farm, and field waste problems.

Ecology: Selected Concepts. David B. Sutton and N. Paul Harmon. xv + 287 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1973. $3.95, paper.

Intended to provide the reader with an understanding of the basic concepts of ecology and the major human implications of these concepts. Intended as a teaching device, the book both asks questions to provoke thought, and answers these questions somewhere in the textual material. It utilizes many graphs, charts, and illustrations in presenting this information.

Pollution Control in the Dairy Industry. Harold R. Jones. ix + 277 pages. Noyes Data Corp., Park Ridge, N.J. 07656. 1974. $24, hard cover.

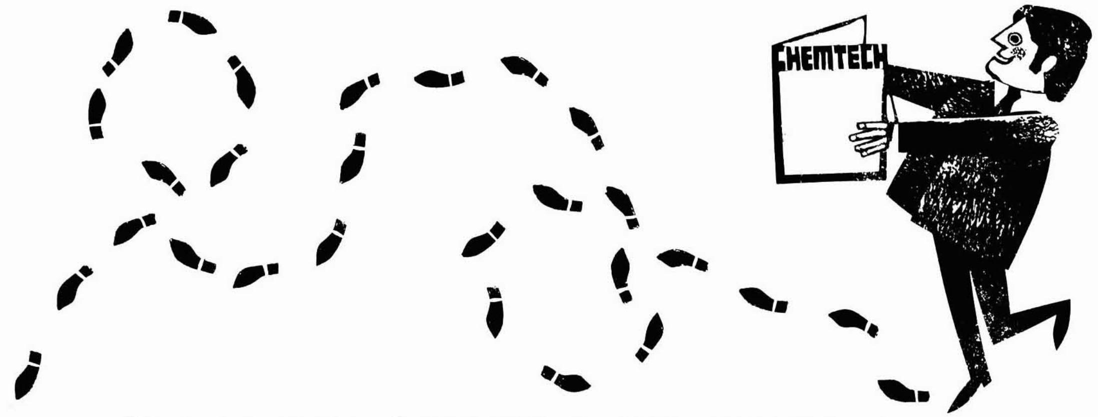
Based on authoritative government reports, book attempts to clarify the ways and means open to the alert dairy processor who must keep his polluting wastes down to a minimum. Important processes are interpreted and explained by actual case histories. It reflects on problems brought about by increasing costs, most stringent effluent discharge requirements, and land limitations because of urbanization.

Environmental Health and Safety. Herman Koren. xxii + 315 pages. Pergamon Press, Inc., Maxwell House, Fairview Park, Elmsford, N.Y. 10523. 1974. $8.75, paper. $16, hard cover.

Makes available information for the design and practice of environmental health and safety programs. It is designed both for the health professional and for the student. The book focuses mainly on the hospital, but its procedures are applicable for other institutions as well. Infection control, patient and employee safety, and special programs and techniques, all are considered.

Plants and Environment: A Textbook of Plant Autecology. 3rd ed. R. F. Daubenmire. ix + 422 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1974. $13.50, hard cover.

Third edition of this textbook deals with autecology, the study of plant ecology that considers the interrelations between the individual plant and its environment. Elucidation of basic principles is the book's primary objective. Attention is given to the choice of pertinent examples, and also to the practical application of ecological principles.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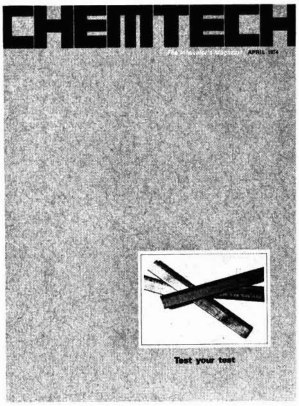
CHEMTECH
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Test your test

MEETING GUIDE

July 29–31 Columbia, Mo.
Nuclear Methods in Environmental Research. American Nuclear Society

Write: David Pettengill, 244 E. Ogden Ave., Hinsdale, Ill. 60521

July 30–August 4 Seattle, Wash.
Intersociety Conference on Environmental Systems. American Society of Mechanical Engineers

Write: ASME, 345 E. 47th St., New York, N.Y. 10017

August 4–9 Rindge, N.H.
Engineering Coal Waste Disposal. Engineering Foundation

Conference on "Urban Runoff-Quantity and Quality" will be held at same location August 11–16. *Write:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 11–14 Syracuse, N.Y.
Annual Meeting. Soil Conservation Society of America

Theme is "Land Use-Persuasion or Regulation?" *Write:* SCSA, 7515 Northeast Ankeny Rd., Ankeny, Iowa 50021

August 18–21 Salt Lake City, Utah
Seventy-eighth National AIChE Meeting. American Institute of Chemical Engineers

Contact: Joel Henry, AIChE, 345 E. 47th St., New York, N.Y. 10017

August 21–23 Ft. Collins, Colo.
Annual Meeting. International Solar Energy Society, U.S. Section

Contact: S. Karaki, Dept. of Civil Engineering, Colorado State U., Ft. Collins, Colo. 80521

August 25–28 San Francisco, Calif.
National Conference on Control of Hazardous Material Spills. American Institute of Chemical Engineers and EPA

Contact: J. Henry, AIChE, 345 E. 47th St., New York, N.Y. 10017

August 26–30 Honolulu, Hawaii
Circum-Pacific Energy and Mineral Resources. American Association of Petroleum Geologists and others

Contact: Dolly Shivers, ASME, 345 E. Halbouty Bldg., 5111 Westheimer Rd., Houston, Tex. 77027

August 26–30 San Francisco, Calif.
Intersociety Energy Conversion Engineering Conference. American Society of Mechanical Engineers

Contact: Dolly Shivers, ASME, 345 E. 47th St., New York, N.Y. 10017

August 29–September 2 New York, N.Y.
Western Division Meeting. National Association of Recycling Industries

Other meetings held at various locations at different times. *Write:* NARI, 330 Madison Ave., New York, N.Y. 10017

September 8–12 Miami Beach, Fla.
Joint Power Generation Conference. American Society of Mechanical Engineers

Write: ASME, 345 E. 47th St., New York, N.Y. 10017

September 9–11 Mystic, Conn.
Transport Mechanisms in the Nearshore Environment. American Geophysical Union

Write: AGU, 1707 L St., N.W., Washington, D.C. 20036

September 10–13 Washington, D.C.
Annual Meeting. American Congress on Surveying and Mapping

Theme is "Responses to Environmental Problems." *Contact:* ACSM, 201 Hutton St., Gaithersburg, Md. 20760

September 16–18 Warrenton, Va.
Symposium on Chemical Kinetics Data for the Lower and Upper Atmosphere. EPA and others

Write: S. W. Benson, CODATA Kinetics Symposium, Stanford Research Institute, 333 Ravenswood Ave., Menlo Park, Calif. 94025

September 17–18 Birmingham, Ala.
Annual Meeting. Southern Section of the Air Pollution Control Association

Program includes sampling techniques in the areas—pulp/paper, ferroalloys, land use, energy, woodworking. *Contact:* Don Meffert, Rust Engineering Co., P.O. Box 101, Birmingham, Ala. 35202

September 22–24 Tulsa, Okla.
American Water Works Association—Southwest & Texas Sections Conference. Water and Wastewater Equipment Manufacturers Association

Write: WWEMA, 744 Broad St., Rm. 3401, Newark, N.J. 07102

September 23–25 Washington, D.C.
Annual Conference. Marine Technology Society

Theme is "National Needs and Ocean Solutions." *Write:* MTS, 1730 M St., N.W., Washington, D.C. 20036

September 25–27 San Antonio, Tex.
North American Conference on Motor Vehicle Emission Control. Texas Air Control Board

Write: H. E. Sievers, TACB, 8520 Shoalcreek Blvd., Austin, Tex. 78758

September 26–27 Chapel Hill, N.C.
National Symposium on Ultimate Disposal of Wastewaters and Their Residual. Triangle Universities and others

Write: Water Resources Research Institute, U. of North Carolina, 124 Riddick Bldg., Raleigh, N.C. 27607

September 30–October 3 Boston, Mass.
Secondary Fiber Pulping Conference. TAPPI

Contact: S. J. Hayes, TAPPI, 1 Dunwoody Park, Atlanta, Ga. 30341

September 30–October 4 New Orleans, La.
Navy Health and Safety Workshop. Dept. of the Navy

Emphasis on federal occupational safety and health and environmental quality. *Write:* W. A. Redman, Jr., Navy Environmental Health Center, 3333 Vine St., Cincinnati, Ohio 45220

October 6–11 Denver, Colo.
1974 WPCF Conference. Water Pollution Control Federation

Contact: Robert Canham, WPCF, 3900 Wisconsin Ave., Washington, D.C. 20016

October 7–10 Chicago, Ill.
Pack Expo 1974. Fibre Box Association

Write: FBA, 224 S. Michigan Ave., Chicago, Ill. 60604

October 14–18 Champaign, Ill.
Precipitation Scavenging. Atomic Energy Commission

Write: R. W. Beadle, Physical and Chemical Transport Program, Div. of Biomedical and Environmental Research, AEC, Washington, D.C. 20545

October 14–19 Denver, Colo.
Annual Meeting. Association of Engineering Geologists

Write: William Rogers, Tech. Program Chairman, Box 15124, Denver, Colo. 80215

October 15–17 Research Triangle Park, N.C.
Seventeenth Biological Safety Conference. Becton, Dickinson, and Co.

Subjects to be covered include NCI guideline for carcinogens, environmental pollution, and OSHA and EPA regulations for biological labs.

Write: L. A. Taylor, B-D Co., P.O. Box 12016, Research Triangle Park, N.C. 27709

(Continued on page 634)

October 16–18 Honolulu, Hawaii
American Water Works Association—California Section Conference. Water and Wastewater Equipment Manufacturers Association

Write: WWEMA, 744 Broad St., Rm. 3401, Newark, N.J. 07102

October 21–23 Madison, Wis.
Lake Protection and Management. EPA and others

Write: Lake Protection & Management Conference, U. of Wisconsin-Extension, 1815 University Ave., Madison, Wis. 53706

October 21–25 Kansas, Mo.
Environmental Engineering Meeting. American Society of Civil Engineers

Write: ASCE, 345 E. 47 St., New York, N.Y. 10017

October 22–24 Louisville, Ky.
Coal and the Environment Exposition. The National Coal Association and others

Contact: M. B. Wolf, P.O. Box 17413, Dulles International Airport, Washington, D.C. 20041

Courses

July 22–24 Boone, N.C.
Environmental Assessment and Impact of Water Resource Development. University of North Carolina

Contact: F. E. McJunkin, Water Resources Research Institute, U. of North Carolina, 124 Riddick Bldg., Raleigh, N.C. 27606

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Industrial Pollution Control. Clemson University

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July 22–26 Ann Arbor, Mich.
Combustion Engine Emissions. University of Michigan

Other courses offered at various dates. *Contact:* U. of Michigan, Continuing Engineering Education, Chrysler Center-N. Campus, Ann Arbor, Mich. 48105

July 29–August 9 Cambridge, Mass.
Energy—A Unified View. Massachusetts Institute of Technology

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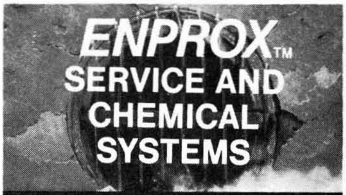

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Jon M. Heuss,[1] George J. Nebel, and Basil A. D'Alleva

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■ The effects of gasoline aromatic and lead content on exhaust hydrocarbon reactivity were separately investigated in a large irradiation chamber. The study emphasized the measurement of eye irritation and of photochemically produced eye irritants, particularly peroxybenzoyl nitrate (PBzN). Adding tetraethyllead (TEL) to an unleaded commercial gasoline did not affect exhaust reactivity. However, adding aromatics to a special low-aromatic gasoline increased the reactivity criteria associated with eye irritation, but had little or no effect on other reactivity criteria such as ozone or NO_2 formation. Isopropyl benzene had the greatest effect, followed by *o*-xylene, *n*-propyl benzene, ethylbenzene, toluene, and benzene. Comparable tests with commercial gasolines failed to show a correlation between eye irritation and total aromatic content of the gasoline. Some of the implications of the results for the blending of future gasolines are discussed.

Regulating gasoline composition to reduce photochemical smog, first suggested in the 1950's, has never been widely adopted. The only known regulation is Rule 63, which limits the olefin content of gasoline sold in Los Angeles County to about 15%. One reason why gasoline composition has not been more widely controlled is the realization that it would have only a limited effect on the composition of auto exhaust, and thus on its photochemical reactivity. It is well known that many of the photochemically reactive hydrocarbons in auto exhaust are not originally present in gasoline but are formed in the engine. Fuel composition, although important, is not the only factor affecting exhaust composition.

Nevertheless, the relationships between fuel composition and exhaust composition have been emphasized in several recent studies (Morris and Dishart, 1971; Wigg et al., 1972; Fleming, 1970; Dimitriades et al., 1970; Ninomiya and Biggers, 1970). These studies have revived interest in fuel composition as an antismog measure. Also contributing to the increased interest has been the discovery by Heuss and Glasson (1968) of peroxybenzoyl nitrate (PBzN), a potent eye irritant formed by irradiating certain aromatic hydrocarbons with nitric oxide. In the first part of the present study, Heuss's and Glasson's work with pure hydrocarbons was extended to auto exhaust. We particularly wanted to know whether PBzN can be formed by irradiating auto exhaust and, if it can, what relationships exist between fuel composition, PBzN, and eye irritation. Accordingly, we blended different aromatic hydrocarbons in a special low-aromatic gasoline and irradiated the hydrocarbons produced from these fuels (plus NO) in a large irradiation chamber. Eye irritation, PBzN, and other reaction products were measured.

The second part of the study concerns the effect of tetraethyllead (TEL) on exhaust reactivity. The TEL content of gasoline is gradually being reduced, and there is considerable speculation whether the transition to unleaded gasoline will affect photochemical smog. One study, by Dimitriades et al. (1970), is often cited to show that it will increase smog. They compared a group of prototype unleaded gasolines with some present-day leaded gasolines and found an average increase of 25% in exhaust reactivity for the unleaded gasolines, which they attributed to their increased aromatic content. We believe that this well-publicized 25% increase is misleading, for two reasons. First, it is based on only one reactivity criterion, the rate of NO_2 formation, which does not always correlate with the more meaningful measures of smog, such as eye irritation or ozone formation (Altshuller, 1970). Second, future unleaded gasolines should not be greatly different in composition from present-day leaded gasolines, since all 1971 and later model cars are designed to operate on lower octane fuel. We believe that a direct lead/no-lead comparison, with no other changes in fuel composition but with more reactivity criteria measured, would be more relevant. Therefore, in the second part of our study, we tested the exhaust from a commercial 91-octane gasoline with and without added TEL. Eye irritation, PBzN, PAN (peroxyacetyl nitrate), ozone, and formaldehyde, as well as the rate of NO_2 formation were measured.

Experimental

The photochemical reactivities of auto exhaust hydrocarbons generated from the different fuels were measured in the GMR smog chamber facility, shown schematically in Figure 1. Inasmuch as the apparatus and procedures have been reported (Tuesday et al., 1965; Heuss and Glasson, 1968; D'Alleva, 1969), they will be described only briefly.

Test Cars and Driving Cycles. Three production-model passenger cars were used in this investigation. Car A was a 1968 model with a 307 CID engine and the standard controlled combustion system to reduce exhaust emissions; car B was a 1966 model with a 389 CID engine and prototype air injection and exhaust recirculation control systems; car C was a 1971 model with a 350 CID en-

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gine and the standard controlled combustion system. Each car had previously been driven several thousand miles to stabilize emissions.

To generate exhaust for the reactivity measurements, the test car was installed on a chassis dynamometer and was automatically driven through a repetitive driving cycle. The PHS-10 cycle, once proposed as a standard exhaust emission test, was used for most of the study because it is a simple, closed cycle that is representative of city-suburban driving. Prior to the development of PHS-10, the "Los Angeles" cycle was used for a few experiments (Tuesday et al., 1965). The two driving cycles are described in Table I.

Exhaust Hydrocarbon Collection and NO_x Removal System. The entire exhaust from the test car was piped directly into a large constant-volume sampler (CVS). After the test car had been thoroughly warmed up, a small portion of the dilute exhaust from the CVS was diverted into the HC-collection/NO_x-removal system. This system separates most of the oxides of nitrogen from the exhaust hydrocarbons, thereby allowing the hydrocarbons to be transferred to the chamber and to be irradiated at a realistic HC/NO_x ratio. Such treatment is necessary because, as is well known, the low HC/NO_x ratio of normal auto exhaust inhibits photochemical reactions which, in turn, makes it difficult to determine differences in hydrocarbon reactivity. (This is especially true for cars with exhaust emission controls.) The HC-collection/NO_x-removal system is shown schematically in Figure 2. It consists of a series of three cold traps and an absorber through which the dilute exhaust is pumped at a rate of about 0.4 cfm. Most of the hydrocarbons and other organics are retained in the cold traps (kept at 32°, 12°, and −200°F), which are subsequently removed, heated to 250°F, and their contents flushed into the chamber with nitrogen. Most of the nitrogen oxides are retained in the absorber (which contains vermiculite impregnated with a solution of 5% $KMnO_4$ and 10% Na_2CO_3) and are discarded. The volatile hydrocarbons pass through the traps and the absorber and go directly into the chamber. The system effectively removes 90-95% of the nitrogen oxides from the exhaust hydrocarbons. The hydrocarbon losses are only about 5%, which is considered tolerable.

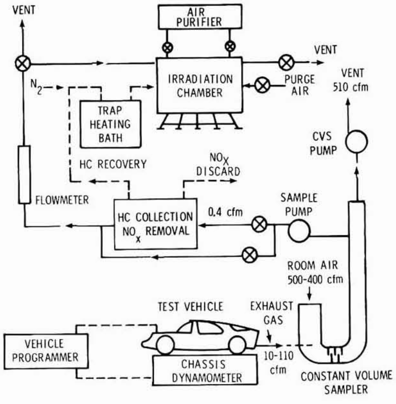

Figure I. GMR smog chamber facility

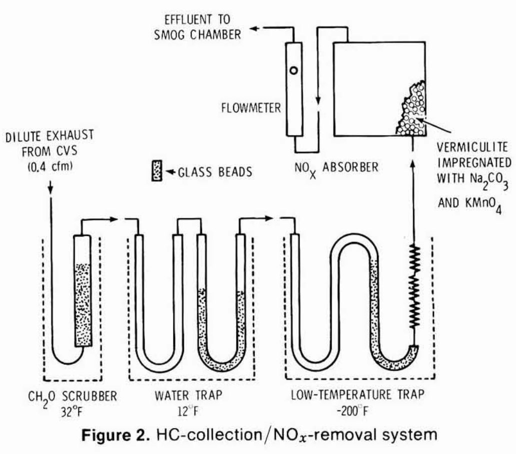

Figure 2. HC-collection/NO_x-removal system

In these experiments, enough exhaust was processed to produce a hydrocarbon concentration of 2.0 ppm C_6 in the chamber. The corresponding NO_x concentration was between 0.2 and 0.4 ppm, but was increased to 1.0 ppm by the addition of nitric oxide. Thus, the concentrations in the chamber at the start of irradiation were 2.0 ppm HC as C_6 and 1.0 ppm NO_x (0.1 to 0.3 ppm NO_2, and the remainder NO).

Irradiation Chamber. The exhaust hydrocarbon-NO_x mixtures were irradiated in a 298-ft^3 stainless steel chamber. Symmetrically spaced inside the chamber are 19 Pyrex lamp tubes, each containing 10 blue fluorescent lamps, two black lamps, and one filtered sunlamp. The radiation intensity within the chamber as measured by the NO_2 photolysis method is 0.4 min^{-1}. Lamp heat is removed by recirculating cooling air through the Pyrex lamp tubes and a water-cooled heat exchanger. The chamber temperature is controlled to ±1°F within the range of 80-100°F by thermostatically regulating the water flow through the heat exchanger. During this investigation, the chamber temperature was maintained at 95°F. A mixing fan and five ports for measuring eye irritation are located along the chamber walls.

Before each run, the chamber air was purified. It was recirculated through a furnace containing a rhodium-alumina catalyst at 950°F for 16 hr at a flow rate of 2 cfm. This treatment reduced the hydrocarbon concentration of

Table I. Driving Cycles

PHS-10

MPH	Time	MPH	Time
Idle	30	52	9
0–19	8	52–37	12
19	15	37	16
19–44	12	37–31	5
44–52	7	31–0	13
			127 sec

Los Angeles

MPH	Time	MPH	Time	MPH	Time
Idle	25.0	30	3.0	Idle	10.5
0–30	13.5	30–40	8.3	0–30	13.5
30–20	7.1	40	3.2	30–20	7.1
20	14.0	40–50	8.3	20–30	8.3
20–10	7.7	50	1.7	30	3.5
10–20	8.3	50–40	8.0	30–40	8.3
20	2.4	40	3.2	40–30	7.7
20–30	8.3	40–30	7.7	30	4.0
30–20	7.1	30	3.0	30–0	12.0
20–30	8.3	30–0	12.0		
					235 sec

the air from, typically, 0.6 ppm C_6 to less than 0.1 ppm C_6. Most of the residual hydrocarbon was methane, which is inert photochemically.

Analytical. The analytical methods used to monitor the reactant and product concentrations are described in Table II. The concentrations were measured both before and during the 5-hr irradiation period. The sample volume withdrawn for analysis was replaced by catalytically purified air that diluted the chamber contents by about 15% at the end of a typical run.

Eye irritation was measured by a panel of eight members. At the end of each run, the panelists exposed their eyes at the eye ports for 4 min. They were instructed to press a timer button when they first experienced any irritation and to rate the intensity at the end of the exposure period. The threshold times were averaged and were converted to a 0 to 10 index by the following formula (Heuss and Glasson, 1968):

$$\text{EI time index} = \frac{240 - t}{240} \times 10$$

where t is the average threshold time in seconds. Similarly, the intensity ratings were assigned numerical values of 0, 1, 2, or 3 for none, light, moderate, or severe. The average of these ratings is called the eye irritation intensity index. Higher numbers on either index indicate more eye irritation.

Photochemical reactivity was judged on the basis of the two eye irritation indexes and on the yields and formation rates of various smog reaction products. As defined in this study, the yield of a product is the maximum concentration attained during the run; the formation rate is one half of the maximum concentration divided by the time (from the start of irradiation) to reach one half of the maximum concentration. Yields will be expressed in parts per million (ppm) and formation rates in parts per billion per minute (ppb/min).

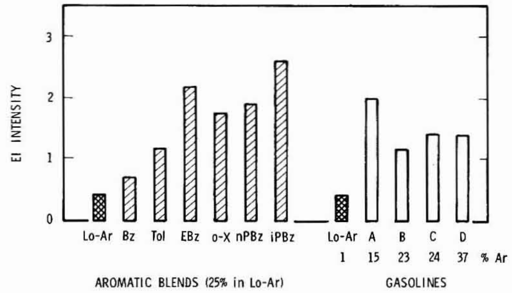

Figure 3. Eye irritation intensity from irradiated auto exhaust

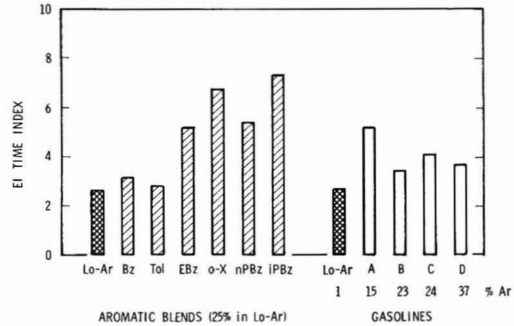

Figure 4. Eye irritation time index from irradiated auto exhaust

Table II. Smog Chamber Analytical Methods

Constituent	Method	Remarks
Total hydrocarbon	Flame ionization	
Individual hydrocarbon	Gas chromatography	McEwen (1966)
Nitrogen oxides	Saltzman	Two automated analyzers, one with dichromate oxidizer
Ozone	Mast	Readings corrected for NO_2 interference
Formaldehyde	Chromotropic acid	Automated analyzer
PAN	Gas chromatography	Electron capture detector; 4-ft glass column packed with 3.8% UC-W98 on 80–100 mesh Diatoport S
PBzN	Gas chromatography	Electron capture detector; 20-in. glass column packed with 3% JXR on 60–80 mesh Gaschrom Q

Table III. Gasoline Composition Data

	% Hydrocarbon (FIA)			Pb, g/gal
	Paraffin	Olefin	Aromatic	
Special gasoline[a]	66	33	1	4.0
Commercial gasoline A	77	8	15	2.5
Commercial gasoline B	69	8	23	2.7
Commercial gasoline C	67	9	24	2.5
Commercial gasoline D	55	8	37	2.1

[a] Same octane and distillation characteristics as commercial gasolines.

Effect of Aromatic Hydrocarbons in Gasoline on Exhaust Hydrocarbon Reactivity

The objective of the first study was to determine the effect of various aromatic hydrocarbons in gasoline on exhaust hydrocarbon reactivity, especially eye irritation. Six aromatics, benzene, toluene, ethylbenzene, *o*-xylene, *n*-propylbenzene, and isopropylbenzene were tested. Each aromatic was blended with a special low-aromatic gasoline in the amount of 25% by volume, about the same aromatic content as the average commercial gasoline. In addition, four commercial gasolines of varying aromatic content were also tested. The hydrocarbon type (FIA) and lead analyses of the special gasoline and of the four commercial gasolines are presented in Table III.

Car A and the PHS-10 driving cycle were used for this portion of the study. Each fuel was tested once. The experimental results are summarized in Table IV and are discussed below.

Eye Irritation. The eye irritation intensity and threshold time results are plotted in Figures 3 and 4, respectively. As shown in Figure 3, very little eye irritation was produced by irradiating the exhaust from the low-aromatic gasoline alone. The intensity index was only 0.4, just slightly above the typical blank value (0.2) for background air. Adding aromatics to the low-aromatic gasoline increased the intensity index in all cases. Benzene had the least effect, followed by toluene, *o*-xylene, *n*-propylben-

Table IV. Effect of Various Aromatics in Gasoline on Exhaust Hydrocarbon Reactivity[a]

Fuel	Photochemical reactivity[b]							
	EI int.	EI time	PBzN	PAN	CH_2O	O_3	R_{O_3}	R_{NO_2}
Gasoline–aromatic blends[c]								
Gasoline only	0.4	2.7	<0.0002	0.21	0.81	0.56	6.3	18.9
Gasoline + benzene	0.7	3.3	<0.0002	0.20	0.63	0.48	3.1	14.5
Gasoline + toluene	1.2	2.8	0.0022	0.18	0.64	0.48	3.7	15.3
Gasoline + ethylbenzene	2.2	5.2	0.0072	0.20	0.79	0.46	4.1	19.3
Gasoline + *o*-xylene	1.8	6.7	<0.0002	0.25	0.77	0.51	4.8	18.4
Gasoline + *n*-propylbenzene	1.9	5.4	0.0088	0.20	0.68	0.46	3.1	15.8
Gasoline + isopropylbenzene	2.6	7.3	0.0070	0.17	0.74	0.53	4.0	14.6
Commercial gasolines								
A (15% Ar)	2.0	5.3	0.0007	0.24	0.72	0.49	4.2	16.1
B (23% Ar)	1.1	3.4	0.0008	0.20	0.66	0.51	3.8	14.0
C (24% Ar)	1.4	4.1	—	—	0.55	0.52	2.4	9.9
D (37% Ar)	1.4	3.7	0.0022	0.19	0.60	0.48	2.5	11.3

[a] Initial concentration: 2.0 ppm HC (C_6); 1.0 ppm NO_x.
[b] Eye irritation intensity 0–3 scale; eye irritation time index 0–10 scale; PBzN, PAN, CH_2O, and O_3 in ppm; R_{O_3} and R_{NO_2} in ppb/min.
[c] 25% (vol) of indicated aromatic in special low-aromatic gasoline.

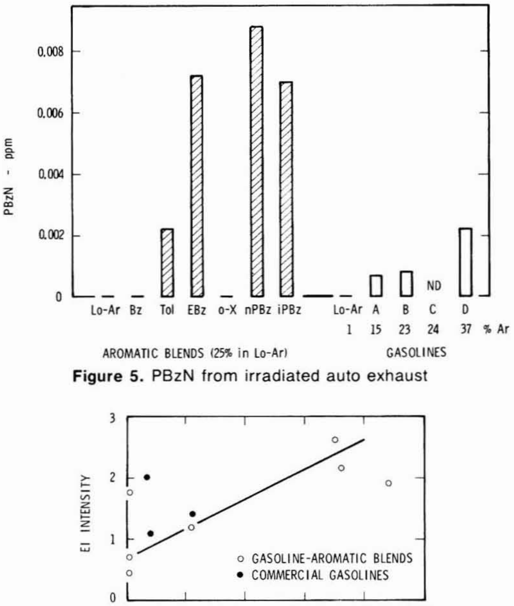

Figure 5. PBzN from irradiated auto exhaust

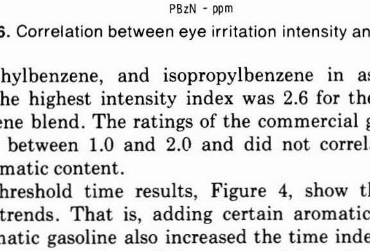

Figure 6. Correlation between eye irritation intensity and PBzN

zene, ethylbenzene, and isopropylbenzene in ascending order. The highest intensity index was 2.6 for the isopropylbenzene blend. The ratings of the commercial gasolines were all between 1.0 and 2.0 and did not correlate with their aromatic content.

The threshold time results, Figure 4, show the same general trends. That is, adding certain aromatics to the low-aromatic gasoline also increased the time index significantly, and the ratings of the commercial gasolines again did not correlate with their aromatic content. Although there were some differences between the two sets of eye irritation results, they are not considered important. (The time index was developed to discriminate between highly irritating mixtures and is not as sensitive as the intensity index for mildly irritative mixtures.) Both the intensity and threshold time results indicate that the important factor affecting eye irritation is the type of aromatics in gasoline, rather than the total quantity of aromatics.

PBzN. The PBzN yields are plotted in Figure 5. Neither the low-aromatic gasoline alone nor the benzene or the *o*-xylene blends produced any detectable PBzN. The ethylbenzene and the two propylbenzene blends formed the most PBzN, between 0.007 and 0.009 ppm; the toluene blend formed considerably less, only about 0.002 ppm. The yields from the commercial gasolines ranged up to 0.002 ppm and generally increased with the aromatic content of the gasoline.

The correlation between the eye irritation intensity index and the PBzN yield, plotted in Figure 6, is only fair, primarily because the *o*-xylene blend and gasoline A produced moderate eye irritation but little or no PBzN.

PAN. All the aromatic blends and all the commercial gasolines produced about the same amount of PAN, approximately 0.20 ppm. The slightly higher-than-average yields from the *o*-xylene blend and gasoline A (0.25 and 0.24 ppm) help to explain the discrepancy in the eye irritation results mentioned above, since PAN is a moderate eye irritant (Stephens et al., 1961).

Formaldehyde. The low-aromatic gasoline produced the most formaldehyde, 0.81 ppm. Adding aromatics to the gasoline decreased the yield by as much as 20% for the benzene and toluene blends. This result was not unexpected since pure hydrocarbon studies have shown that aromatics, as a class, produce less formaldehyde than do paraffins or olefins. The formaldehyde yields from the commercial gasolines ranged from 0.55 to 0.72 ppm and generally decreased with the aromatic content of the gasoline.

Ozone. The ozone yields ranged from 0.46–0.56 ppm. There was little difference between fuels, although the low-aromatic gasoline formed slightly more ozone than any of the aromatic blends or any of the commercial gasolines. The ozone formation rates, plotted in Figure 7, ranged from 2.4–6.3 ppb/min. The ozone rate was noticeably higher for the low-aromatic gasoline than for any of the other fuels.

Nitrogen Dioxide. The NO_2 formation rates are plotted in Figure 8. Except for ethylbenzene, adding aromatics to the low-aromatic gasoline reduced the NO_2 formation rate. The NO_2 rates for the commercial gasolines were generally lower than for the aromatic blends and decreased with increasing aromatic content. The latter is contrary to the finding of Dimitriades et al. (1970) that increasing the aromatic content of gasoline increases exhaust reactivity (NO_2 rate). One possible explanation for this discrepancy is that the two investigations were conducted at different HC/NO_x ratios—12:1 in ours and only 3:1 in theirs. It is well known that the HC/NO_x ratio affects photochemical reactivity and that mixtures with higher ratios are more reactive. Thus, different hydrocarbons may rank in different order depending upon the HC/NO_x ratio at which they are irradiated. Another possible explanation is that the gasolines in the two investigations were vastly different. Since the specific hydrocarbons in gasoline probably have more effect on exhaust reactivity than the total of any one type, any correlation between exhaust reactivity and the total aromatic content of gasoline may be coincidental.

Eye Irritant Precursors. Without additional information we cannot tell whether the differences in eye irritation previously discussed were primarily due to the fuel aromatics present in the exhaust or to other aromatic hydrocarbons or aldehydes formed in the engine. Some knowledge of the exhaust hydrocarbon composition and of the eye irritation produced by individual hydrocarbons is needed. The detailed hydrocarbon analyses are not available, but individual hydrocarbon eye irritation data are (Heuss and Glasson, 1968). Comparing them with the exhaust hydrocarbon eye irritation values should enable us to tell whether the exhaust hydrocarbons are, on the average, more or less reactive than the parent compounds.

The two sets of eye irritation data are compared in Table V. The first column lists the aromatic hydrocarbon tested; the second column, the eye irritation produced by irradiating the pure aromatic; and the third column, the eye irritation produced by irradiating the exhaust hydrocarbons from the gasoline blend containing 25% of the aromatic. Both studies were made at the same HC and NO_x concentrations, so they are directly comparable. The greatest difference in Table V is between pure isopropylbenzene and the exhaust hydrocarbons from the fuel containing isopropylbenzene. Pure isopropylbenzene produced very little eye irritation when irradiated (with NO), but the exhaust hydrocarbons from the isopropylbenzene–gasoline blend produced very strong eye irritation. The exhaust hydrocarbons from the ethylbenzene–, *o*-xylene–, and benzene–gasoline blends were also more irritating than the pure compounds, but the differences were not so great as with isopropylbenzene. These four aromatics must form some exhaust products that produce more eye irritation than the parent compounds when irradiated. On the other hand, the exhaust hydrocarbons from the toluene– and the *n*-propylbenzene–gasoline blends were less irritating than the pure compounds. These two aromatics must form exhaust products that, on the average, produce less eye irritation than the parent compounds.

Table V. Eye Irritation from Irradiated Aromatic Hydrocarbons and from Irradiated Auto Exhaust Derived from Aromatic–Gasoline Fuel Blends

	Eye irritation intensity[a]	
Aromatic hydrocarbon	Pure hydrocarbon[b]	Auto exhaust[c]
Isopropylbenzene	0.6	2.6
Ethylbenzene	1.6	2.2
n-Propylbenzene	2.5	1.9
o-Xylene	0.9	1.7
Toluene	2.0	1.2
Benzene	0.2	0.7

[a] 0–3 scale. [b] HC 2.0 ppm; NO_x 1.0 pm (Heuss and Glasson, 1968). [c] HC 2.0 ppm C_6; NO_x 1.0 ppm (this study).

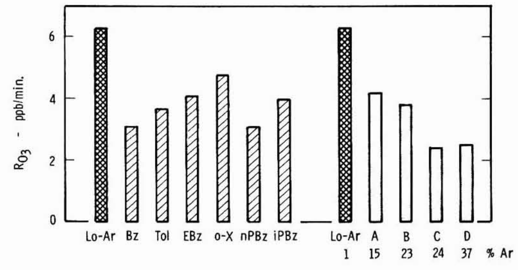

Figure 7. Rate of ozone formation in irradiated auto exhaust

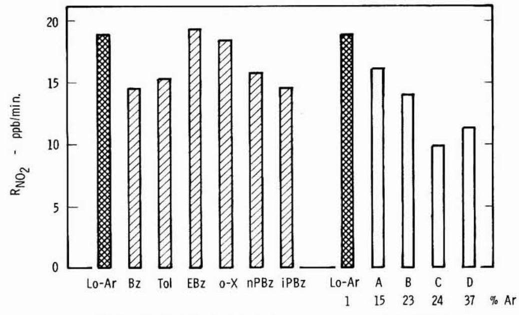

Figure 8. Rate of NO_2 formation in irradiated auto exhaust

A few experiments were made to identify the hydrocarbons formed in the engine that might have an important effect on eye irritation. Isopropylbenzene and toluene were selected for study because they showed the greatest differences in the pure hydrocarbon exhaust comparison (Table V). Blends of 40% toluene in isooctane, 40% isopropylbenzene in isooctane, and pure isooctane were tested. Car B and the Los Angeles driving cycle were used for these experiments. This car produces relatively little NO_x, so it was not necessary to employ the trapping system. The exhaust was simply diluted with clean air and passed directly into the irradiation chamber. No extra NO was added.

The concentrations of individual hydrocarbons in the chamber before irradiation and the eye irritation after irradiation are shown in Table VI. The total HC and NO_x concentrations and the HC/NO_x ratios are also shown. The HC/NO_x ratio of the isooctane exhaust was much higher than for the two aromatic blends, but this is not considered important because there was almost no eye irritation from the isooctane–exhaust hydrocarbons. On the other hand, the exhaust hydrocarbons from the aromatic blends were very irritating. Most of the eye irritation from the toluene–isooctane blend can be attributed to the toluene in the exhaust. The concentrations of the reactive light olefins were only slightly greater than for pure isooctane, and unreactive benzene was the only new aromatic hydrocarbon found. The very strong eye irritation from the isopropylbenzene–isooctane blend must have been caused by the small amounts of styrene and methyl styrene in the exhaust, both of which rate high on the eye irritation reactivity scale and form PBzN in good yield when irradiated (Heuss and Glasson, 1968). We suspect that the styrenes and other aromatic olefins are important combustion-derived hydrocarbon precursors in exhaust from commercial gasolines. We also suspect that benzaldehyde is an important precursor since it has been found in the exhausts from aromatic fuels (Ninomiya and Biggers, 1970) and since it is an intermediate in the production of PBzN from aromatic hydrocarbons (Heuss and Glasson, 1968). However, benzaldehyde was not determined in this investigation.

All these studies suggest that it may be possible to reduce the eye irritation aspects of photochemical smog by restricting the amounts of certain aromatics in gasoline. At this time, however, not enough is known about the complex relationships between gasoline composition and exhaust composition to establish the usefulness of this approach.

Table VI. Individual Hydrocarbons in Dilute Exhaust from Various Fuels

Before irradiation, ppm	Isooctane	Isooctane(60) toluene(40)	Isooctane(60) isopropyl-benzene(40)
Methane	0.75	0.57	0.59
Isooctane	0.73	0.46	0.42
Other paraffins	0.13	0.05	0.09
Acetylenes	0.23	0.37	0.37
Ethylene	0.17	0.26	0.23
Propylene	0.21	0.22	0.20
C_4 olefins	0.29	0.30	0.27
Other olefins	0.02	0.03	0.02
Benzene		0.09	0.06
Toluene		0.77	0.02
Styrene			0.09
α-Methyl styrene			0.03
Isopropylbenzene			0.40
Other aromatics			0.03
Total HC as C_6	1.68	2.29	2.16
Total NO_x	.28	1.06	1.13
HC as C_1/NO_x	36	13	11
	After Irradiation		
EI intensity, 0–3 scale	0.3	2.1	2.7
EI time index, 0–10 scale	1.9	4.9	6.7

Effect of Tetraethyllead in Gasoline on Exhaust Hydrocarbon Reactivity

The objective of this portion of the study was to determine the direct effect of tetraethyllead (TEL) on exhaust hydrocarbon reactivity. A commercial, unleaded 91-octane gasoline was tested with and without added TEL (2.3 grams Pb per gallon from Motor Mix). Car C and the PHS-10 driving cycle were used.

The results are presented in detail in Table VII. Each fuel was tested five times. The target hydrocarbon and nitrogen oxide concentrations were 2.0 and 1.0 ppm, respectively. Although it is not shown in Table VII, it was necessary to process more exhaust when using unleaded fuel to attain the same hydrocarbon concentration in the chamber (about 24 ft^3 vs. 22 ft^3 for leaded fuel). This indicates that the exhaust hydrocarbon concentration was about 8% higher with leaded fuel than with the same fuel without lead. Other investigators have also observed this "direct lead" effect (Leikkanen and Beckman, 1971).

The presence or absence of lead in gasoline had no significant effect on any of the seven reactivity criteria, as indicated by the low F values at the bottom of Table VII. The F values, calculated by conventional analysis of variance techniques, are all well below the critical value of 5.32 for 95% confidence. The seven reactivity criteria are compared graphically in Figure 9 on a relative (unleaded = 1.00) basis. None of the differences indicated are significant.

In addition to PBzN, PAN, and formaldehyde, a fourth eye irritant, acrolein, was measured during some of these runs. With either leaded or unleaded fuel, the acrolein concentration in the chamber decreased from about 0.03 ppm initially, to about 0.015 ppm after 5 hr of irradiation. This suggests that acrolein may not be an important eye irritant in photochemical smog if, as in these experiments, it decomposes in the atmosphere faster than it forms.

Finding no significant differences between the tests with leaded and unleaded gasolines, we concluded that TEL, per se, had no detectable effect on the photochemical reactivity of exhaust hydrocarbons in this series of ex-

Table VII. Effect of Tetraethyllead in Gasoline on Exhaust Hydrocarbon Reactivity

Initial concn ppm				Photochemical reactivity[a]						
$HC(C_6)$	NO_x[b]	CH_2O	EI int.	EI time	PBzN	PAN	CH_2O	O_3	R_{NO_2}	R_{O_3}
				Unleaded Gasoline						
2.29	1.01	0.11	0.85	2.67	0.0018	0.09	0.39	0.40	14.1	2.71
2.18	0.97	0.11	0.86	1.71	0.0022	0.11	0.49	0.34	17.7	3.33
2.13	0.99	0.11	1.05	3.25	0.0020	0.11	0.47	0.36	17.9	3.03
2.07	1.02	0.10	0.56	1.96	0.0017	0.09	0.45	0.38	18.2	2.90
2.23	1.00	0.10	0.72	2.79	0.0018	0.10	0.46	0.38	17.5	3.25
Av. 2.18	1.00	0.11	0.81	2.48	0.0019	0.10	0.45	0.37	17.1	3.04
				Leaded Gasoline[c]						
2.30	1.06	0.08	1.31	3.54	0.0017	0.11	0.44	0.35	16.6	3.07
2.12	1.01	0.08	0.75	2.00	0.0020	0.13	0.44	0.34	16.3	3.01
2.01	1.15	0.10	0.57	1.29	0.0022	0.10	0.46	0.35	16.5	2.52
2.24	1.05	0.07	0.94	3.25	0.0025	0.09	0.48	0.37	17.3	3.34
2.16	1.09	0.09	1.06	2.92	0.0027	0.10	0.47	0.38	16.7	3.25
Av. 2.17	1.07	0.08	0.93	2.60	0.0022	0.11	0.46	0.36	16.7	3.04
Standard error[d]			0.24	0.80	0.0003	0.01	0.03	0.02	1.2	0.29
F ratio			0.61	0.06	2.60	0.54	0.10	1.24	0.27	0.00

[a] Eye irritation intensity 0–3 scale; eye irritation time index 0–10 scale; PBzN, PAN, CH_2O, and O_3 in ppm; R_{O_3} and R_{NO_2} in ppb/min. [b] About 80% NO and 20% NO_2. [c] Same unleaded gasoline plus 2.3 grams Pb per gallon from Motor Mix. [d] Square root of the residual mean square.

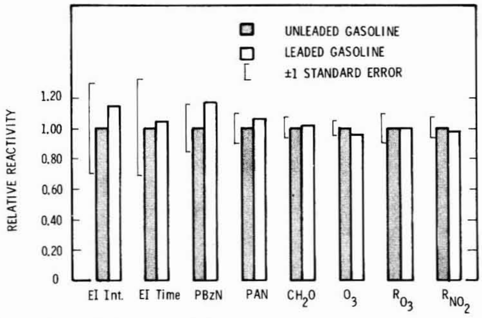

Figure 9. Relative reactivity of irradiated auto exhaust from leaded and unleaded gasoline

periments. This is essentially the same conclusion reached by Morriss et al. (1958). It also helps to clarify the often-quoted conclusion of Dimitriades et al. (1970) that the transition from present-day leaded gasolines to future unleaded gasolines will increase exhaust reactivity (as measured by the rate of NO_2 formation) by as much as 25%. In the Dimitriades study, the leaded and unleaded gasolines were different in composition and, presumably, the increases in reactivity were due to the higher aromatic content of the unleaded gasolines rather than to the absence of lead.

Sturm and Dimitriades (1973) extended these studies to include PAN and oxidant measurements. They concluded that the emissions from prototype unleaded gasolines were more reactive than those from present-day (pre-1971) leaded gasolines when measured by oxidant dosage or PAN dosage as well as by the rate of NO_2 formation. It is difficult to compare their results with ours, however, because Sturm and Dimitriades irradiated mixtures of exhaust and evaporative emissions. Nevertheless, we believe it significant that Sturm and Dimitriades attributed the reactivity differences they measured to the higher content of aromatics and of C_4-C_5 olefins in their unleaded fuels rather than to the absence of lead. This agrees with our conclusion that the effect of TEL on the composition of exhaust hydrocarbons, if any, is too small to affect their photochemical reactivity.

Summary and Conclusions

The presence or absence of TEL in gasoline did not affect the photochemical reactivity of the exhaust hydrocarbons produced from the gasoline. Therefore, the transition from leaded to unleaded gasoline, now under way, should have no effect on the photochemical reactivity of exhaust hydrocarbons generally, as long as the unleaded gasolines of the future are not greatly different in composition from present-day gasolines.

Peroxybenzoyl nitrate (PBzN) was formed in ppb amounts by irradiating auto exhaust in laboratory apparatus. Thus, it is likely that PBzN is also formed in the atmosphere and is an important eye irritant in photochemical smog.

Certain aromatics, when added to a low-aromatic gasoline, greatly increased the eye irritation and PBzN yield of the exhaust hydrocarbons produced from the gasoline, although they did not increase other reactivity criteria, such as ozone, PAN, formaldehyde, or the NO_2 formation rate. The six aromatics tested can be ranked in the following order for their effect on eye irritation:

$$\text{isopropylbenzene} > \left\{\begin{array}{l} o\text{-xylene} \\ n\text{-propylbenzene} \\ \text{ethylbenzene} \end{array}\right\} > \text{toluene} > \text{benzene}$$

In the case of isopropylbenzene, aromatic olefins formed during combustion appear to be important eye irritant precursors.

The eye irritation produced by four commercial gasolines, similarly tested, did not correlate with their total aromatic content. This is further evidence that the specific aromatics in gasoline, not the total, is the important factor affecting eye irritation.

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Received for review October 30, 1972. Accepted February 11, 1974. Presented at 163rd American Chemical Society National Meeting, Boston, Mass., April 9-14, 1972.

Characteristics of Laminar Jet Impactors

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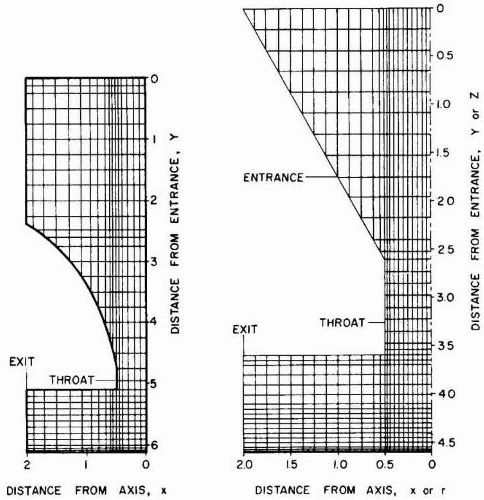
■ The characteristics of rectangular and round impactors have been determined by the numerical solution of the Navier-Stokes equations and of the equation of motion of the particles. The numerical method was verified by comparing the predicted point of particle impact with impact points determined experimentally. The effect of jet-to-plate distance, jet Reynolds number, and jet throat length on the characteristic impactor efficiency curves has been studied. The jet throat length was found to have a negligible influence, but the Reynolds number has a substantial effect below a value of about 500. The effect of the jet-to-plate distance is small above a value of 1.5 jet widths and 1.0 jet diameter for the rectangular and found impactors, respectively. Thus, actual impactors should be designed with jet-to-plate distances above these critical values to ensure that slight changes in this distance will not significantly influence the cut-off particle diameter of the impactor.

Inertial impactors have been used extensively for collecting airborne particles for gravimetric or chemical analysis. They have been used in air quality monitoring, in stack sampling, and in other applications where the unique ability of the impactor to collect and separate airborne particles into finite size ranges is desired.

Many impactors have been described in the literature, but only a few theoretical impactor studies have been made. In two previous papers Marple et al. (1973 and 1974) summarized these previous theoretical and experimental studies and described a mathematical method for determining the flow field in impactors. The method is based on the numerical solution of the Navier-Stokes equation and is applicable to both the two-dimensional flow field of the rectangular impactor and the axi-symmetrical flow field of the round impactor. The method can be applied to any impactor of a specified geometric contour, and the flow field can be determined to a high degree of accuracy, the ultimate accuracy being limited only by the availability of computer time.

The solution of the full Navier-Stokes equation with no simplifying assumptions has made it possible to obtain actual flow fields in inertial impactors theoretically. Thus parameters affecting the operation of the inertial impactor, such as Reynolds number, jet-to-plate distance, and jet throat length, can now be studied theoretically and systematically and their effect on the impactor operating characteristics determined. Previously, these parameters could only be studied empirically, and the results were not always consistent, because of experimental difficulties.

This paper is concerned with impactor performance based on particle trajectory calculations using the previously determined flow fields. The theoretical results are then verified experimentally and compared with data reported in the literature.



(a) (b)

Figure 1. Impactor contour and grid pattern used in numerical solution

(a) Rectangular impactor used in the theoretical and experimental point-of-impact studies. (b) Round and rectangular impactors used in all theoretical calculations

Particle Trajectory Calculations

Figure 1a is a schematic diagram of the impactor contour and the system of grid lines used in the numerical solution of the Navier-Stokes equation reported previously. The stream function and the velocity components at each of the node points on this grid are known after the relaxation solution of the finite difference equations has converged in the computer solution. To calculate the particle trajectory through the rectangular impactor, we can use the known flow field and the equations of motion of the particle in the x-y coordinate,

$$m\frac{d^2x'}{dt'^2} = \frac{3\,\pi\mu D_p}{C}\left(V_x' - \frac{dx'}{dt'}\right) \tag{1}$$

$$m\frac{d^2y'}{dt'^2} = \frac{3\,\pi\mu D_p}{C}\left(V_y' - \frac{dy'}{dt'}\right) \tag{2}$$

which can be written in dimensionless form as follows:

$$\frac{\text{St}}{2}\,\frac{d^2x}{dt^2} = V_x - \frac{dx}{dt} \tag{3}$$

$$\frac{\text{St}}{2}\,\frac{d^2y}{dt^2} = V_y - \frac{dy}{dt} \tag{4}$$

$$\text{St} = \frac{\rho_p C V_0 D_p^2}{9\,\mu\text{W}} \tag{5}$$

where the Stokes number, St, is defined (Fuchs, 1964, p 154) as the ratio of the particle stopping distance to the half-width of the impactor throat, $W/2$. The square root of the Stokes number, $\text{St}^{1/2}$, is used here as a measure of the dimensionless particle size.

Equations 3 and 4 have been integrated using a Runge-Kutta fourth-order method of integration. The two equa-

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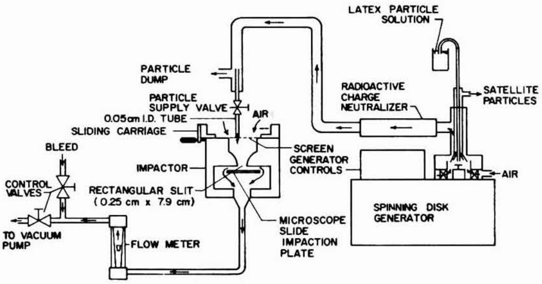


Figure 2. Apparatus for point-of-impact studies

tions must be integrated simultaneously, since the components of the fluid velocity, V_x and V_y, are dependent on the position of the particle.

The integration process is started by first assigning a specific Stokes number to a particle, and giving it an initial velocity equal to the local fluid velocity of the fluid at the starting position at the entrance. By use of the Runge-Kutta integration method, the movement of the particle, Δx and Δy, during a small increment of time, Δt, is determined. This gives the position of the particle at the end of the time increment. This process is then repeated, and the movement of the particle through the impactor is followed until the particle either impacts on the plate or exits through the impactor exit. A detailed description of the numerical procedure and the computer program used has been given by Marple (1970).

As the particle comes near the impaction plate, one of two methods can be used to determine whether the particle will impact. If the point of impact on the plate or the velocity of impact is needed, the motion of the particle must be followed through until final impaction has occurred. A particle is considered to have impacted if its center has come to a distance of one particle radius from the plate. The particle radius is given by

$$\frac{r_p}{W} = \sqrt{\frac{9\ \mathrm{St}\mu}{4\ \rho_p V_o C W}} \tag{6}$$

which is obtained from Equation 5. However, in many cases, it is only necessary to decide whether a particle will actually impact, given its position and velocity components at a point sufficiently close to the plate. In such cases, considerable computer time will be saved if the analytical criteria given in the Appendix are used, since further integration of the equation of motion then becomes unnecessary.

Experimental Point-of-Impact Studies

To verify the results of the trajectory calculations, a special impactor was constructed. This impactor, shown schematically in Figure 2, differs from the conventional impactor in that the aerosol is introduced as a narrow stream into the impactor, and the point of entry along the inlet can be adjusted by means of a micrometer attached to the small aerosol inlet tube (i.d. = 0.05 cm). By moving the aerosol inlet tube along the entrance and measuring the corresponding point of impact of the particles on the impaction plate, we can determine the end points of the particle trajectories and compare them with the theoretical calculations.

To prevent particle bounce on the impaction plate, an adhesive coating was applied to the glass microscope-slide impaction plate. Several coatings reported in the literature were tried, but the one found to be most satisfactory was prepared from a 1% solution of 100,000 cs Dow-Corning DC-200 silicone oil dissolved in hexane (McFarland and Husar, 1967). Several drops of the solution were placed on the microscope slide and spread into a thin film. After the solvent had evaporated from the liquid film, a thin adhesive coating of the silicone oil was left on the slide, and this film was very effective in preventing particle bounce.

The particles used in these studies were polydisperse 6- to 14-μm diameter styrene-divinylbenzene spheres obtained from the Dow Chemical Co. (Midland, Mich.). The density of these particles is 1.050 g/cc, according to the manufacturer. The particles were aerosolized by means of a spinning-disk aerosol generator, and then passed through a Kr-85 radioactive charge neutralizer to neutralize the particle electrostatic charge.

To determine the point of impact, the aerosol inlet tube was placed at a distance X_c from the center line and the aerosol inlet valve was momentarily opened to allow some particles to enter the impactor. The aerosol inlet was then moved to the same distance, X_c, on the other side of the center line, and another sample was similarly taken. The microscope slide impaction plate was then removed from the impactor and examined and photographed in an optical microscope. From the photomicrographs, the point of impact of the particles and the particle diameter were measured and compared with the theoretical calculations.

Figure 3 shows the results of three such point-of-impact studies. The results were obtained for a Reynolds number

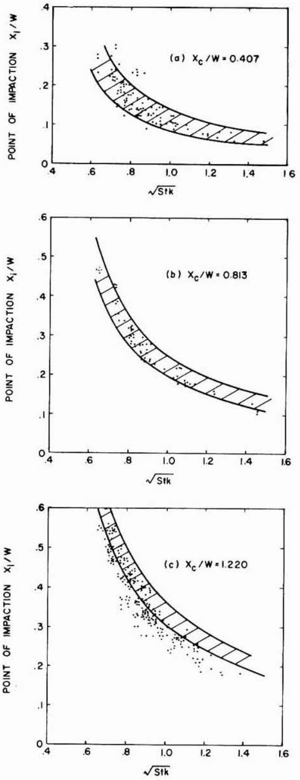


Figure 3. Comparison of theoretical and experimental impaction points in the variable point impactor for Re = 2000 and particle starting points at (a) x_c/w = 0.407, (b) x_c/w = 0.813, and (c) x_c/w = 1.220

● Styrene-divinylbenzene latex particles; shaded area is impaction region predicted by theory of 2000 and three X_c/W values: 0.407, 0.813, and 1.220. It should be noted that larger particles with a higher Stokes number impacted closer to the center line, as the theory would predict. The shaded areas bounded by the two curves are the theoretically predicted areas of impaction. Finite areas of impaction are predicted by the theory because of the finite size of the aerosol inlet tube.

The agreement between theory and experimental data is seen to be very good for the two X_c/W ratios of 0.407 and 0.813. However, for $X_c/W = 1.220$, there is some discrepancy between the theoretical and experimental results. The cause of this discrepancy is not entirely clear, but it was probably the slight deflection of the aerosol stream as it entered the impactor. This deflection was observed in separate studies in which a dense smoke was introduced through the aerosol inlet. The aerosol stream would deflect toward the curved impactor entrance when it was sufficiently close to the wall.

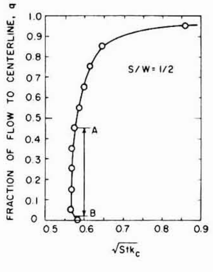
Impactor Efficiency Calculations

In the usual application of the inertial impactor one of the most important impactor characteristics is the efficiency of sampling, defined as the fraction of particles of a certain size that are removed from the aerosol stream by the impaction process.

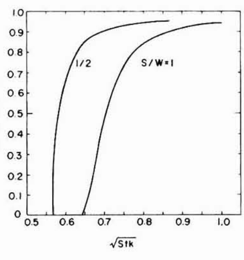
To construct an impactor efficiency curve, the value of the critical Stokes number must be known as a function of the starting position of the particles at the impactor entrance. For particles starting at a specific point at the entrance, there is a minimum Stokes number below which particles will not impact. Thus, for impactor efficiency calculations, the critical Stokes number must be calculated as a function of the particle starting position at the entrance.

To determine the critical Stokes number for a specific entrance position, a specific Stokes number is first assigned to a particle starting at that point. The motion of the particle through the impactor is then followed to determine whether impaction would occur. If impaction occurs, the Stokes number is reduced and the particle motion similarly followed. Conversely, if impaction does not occur, the Stokes number is increased and the particle motion followed. By means of this procedure the critical Stokes number can be determined to any specified accuracy. In these calculations the critical Stokes number was determined to an accuracy of ±0.002.

In Figure 4a, the calculation results for the critical Stokes number as a function of the particle starting position are shown for an impactor operated at $S/W = 0.5$ and a Reynolds number of 1000. The starting position of the particle is specified by the quantity q, where q is the ratio of the volumetric flow between the starting point and the center line to the total flow through the impactor. The quantity, q, is a unique function of the value of the stream function at the starting point. The corresponding impactor efficiency based on these critical Stokes number values is shown in Figure 4b. The point of zero efficiency on Figure 4b corresponds to the minimum Stokes number point on Figure 4a. As the figures show, the minimum critical Stokes number has a value at $\mathrm{St}^{1/2} = 0.568$. To determine the efficiency of the impactor at $\mathrm{St}^{1/2} > 0.568$, a vertical line is drawn, as in Figure 4a, and the points of intersection of this vertical line with the critical Stokes number curves are determined. The impactor efficiency is then equal to the ratio of the flow between points A and B to the total flow through the impactor. For example, at $\mathrm{St}^{1/2} = 0.575$, the calculated efficiency is equal to 0.43 by the above method.

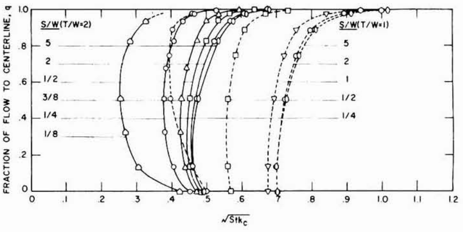


(a) CRITICAL STOKES NUMBERS

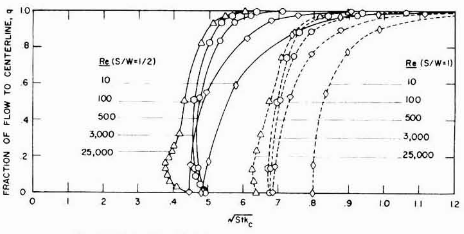


(b) IMPACTOR EFFICIENCY

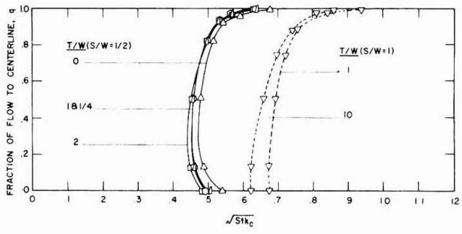
Figure 4. (a) Critical Stokes number as a function of particle entrance position. (b) Impactor efficiency curve for the retangular impactor used in the point-of-impact studies for Re = 1000



(a) EFFECT OF JET-TO-PLATE DISTANCE (Re = 3,000)



(b) EFFECT OF JET REYNOLDS NUMBER (T/W = 1)



(c) EFFECT OF THROAT LENGTH (Re = 3,000)

Figure 5. Critical Stokes number for the rectangular (broken line) and the round (solid line) impactors showing the effect of jet-to-plate distance, Reynolds number and throat length

If the critical Stokes number curve is a monotonic increasing function of the quantity, q, then this curve will be identical to the impactor efficiency curve. This is the case for the efficiency curve for $S/W = 1$, shown in Figure 4b. However, in other cases (for example, $S/W = 1/2$), particles will impact only between the points A and B for a specific Stokes number, and the critical Stokes number curve and the efficiency curves of the impactor are not identical.

Results

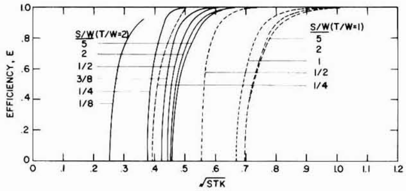
The theoretical procedures described above can be used to determine the impaction curves for rectangular impactors. The same procedures can be applied to a round impactor with axi-symmetrical flows if the coordinates, x and y, are replaced by the corresponding coodinates, r and z, for the round impactor and the equations are suitably modified.

By use of the geometrical contour and the grid pattern shown in Figure 1b, the effect of jet-to-plate distance, jet throat length, and jet Reynolds number has been studied for both the rectangular and the round impactors. The critical Stokes number is shown in Figure 5 as a function of the starting position of the particles at the impactor entrance, and the corresponding impactor efficiency curves are shown in Figure 6.

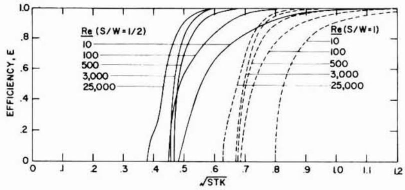
In Figure 6a the efficiency curves for both the rectangular and the round impactors are shown for a Reynolds number of 3000, T/W ratios of 1 and 2, and several S/W ratios, where T is the jet throat length, S is the jet-to-plate distance, and W is the jet width or diameter. From this figure the following three conclusions can be drawn: Round impactors require smaller Stokes numbers for particles to impact than do rectangular impactors at corresponding jet-to-plate distances; the slope of the efficiency curve, which provides a measure for the "sharpness of cut" of a given impactor, is similar for both the rectangular and the round impactors; and the jet-to-plate distance has a significant influence on the position of the impactor efficiency curve along the $St^{1/2}$ axis only at small jet-to-plate distances.

The effect of jet-to-plate distance on the impactor characteristics is shown more clearly in Figure 7, where the value of $St^{1/2}$ at the 50% efficiency point is shown as a function of the jet-to-plate distance. For the rectangular impactor, $St_{0.50}{}^{1/2}$ drops sharply with decreasing jet-to-plate distance below $S/W = 1.5$ and for the round impactor, below $S/W = 1.0$. The experimental points shown in Figure 7 have been taken from the paper by Mercer and Stafford (1969) for the round impactor and from the paper by Mercer and Chow (1968) for the rectangular impactor. The agreement between theory and experiment is seen to be good, although there is a considerable scatter in the experimental data points for the rectangular impactor.

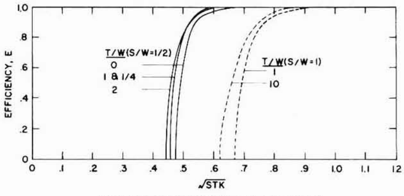
Figure 8 shows a more detailed comparison of the impactor efficiencies for the round impactor again based on the experimental data of Mercer and Stafford for several jet-to-plate distances ranging from 3/8 to 5. The agreement is seen to be exceptionally good. This gives confidence in



(a) EFFECT OF JET TO PLATE DISTANCE (Re=3,000)

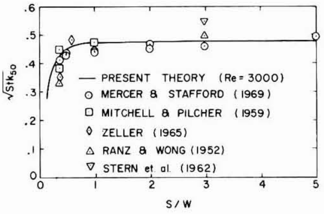


(b) EFFECT OF JET REYNOLDS NUMBER (T/W=1)

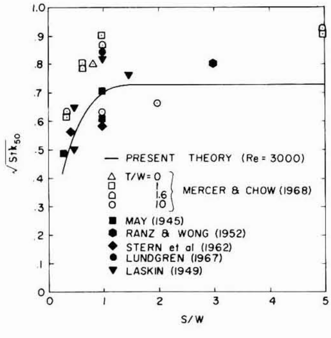


(c) EFFECT OF THROAT LENGTH (Re=3,000)

Figure 6. Impactor efficiency curves for the rectangular (broken line) and the round (solid line) impactors showing the effect of jet-to-plate distance, Reynolds number and throat length



(a) ROUND IMPACTOR



(b) RECTANGULAR IMPACTOR

Figure 7. Theoretical and experimental value of $(Stk_{50})^{1/2}$ as a function of jet-to-plate distance

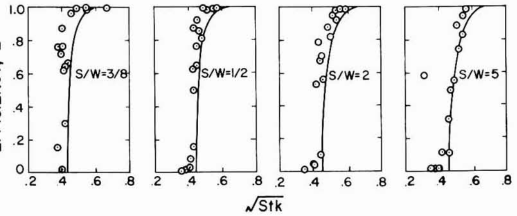
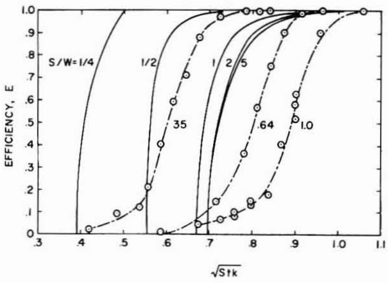
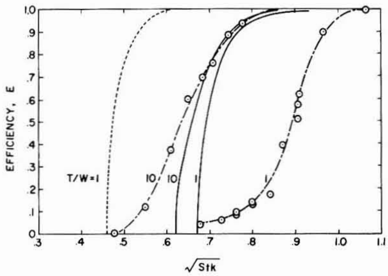


Figure 8. Theoretical and experimental efficiencies of the round impactor

— Theoretical results from the present work; ⊙ experimental data from Mercer and Stafford, 1969



(a) INFLUENCE OF JET-TO PLATE DISTANCE (T/W=1)



(b) INFLUENCE OF THROAT LENGTH (S/W=1)

Figure 9. Theoretical (solid line) and experimental (⊙, Mercer and Chow, 1968) efficiencies of the rectangular impactor at Re = 3000 (broken line for round impactor shown for comparison)

the validity of both the experimental data of Mercer and Stafford and the theoretical procedure developed in the present study.

A similar comparison of the theoretical results with the experimental data of Mercer and Chow (1968) for the rectangular impactor is shown in Figure 9a. The discrepancy is seen to be substantial.

One possible explanation for this discrepancy is provided by the observation of Mercer and Chow, who found a considerable difference between the impactor efficiency curve for a rectangular impactor with a short throat length ($T/W = 1$) and that for a similar impactor with a longer throat length ($T/W = 10$). However, theoretical calculations using the procedure described in this paper give results that are not greatly different for these two cases (see the theoretical and experimental results shown in Figure 9b). This suggests that there were some flow irregularities in the short-throated impactor which Mercer and Chow used and that these irregularities were subsequently damped out by the longer throat length. It should be noted that there is good agreement between the theoretical and the experimental efficiencies for the impactor with the longer throat length, particularly at the upper end of the curve. The discrepancy at the lower end of the curve probably can be attributed to the end effects resulting from the expansion of flow near the ends of the rectangular slit. These expansions would cause the rectangular impactor to behave more like a round impactor at low Stokes numbers since a round impactor requires a lower Stokes number than does a rectangular slit impactor to begin particle impaction. This is seen to be the case in Figure 9b, where the experimental efficiency for the rectangular impactor with $T/W = 10$ begins to rise from zero at a Stokes number close to that for the round impactor.

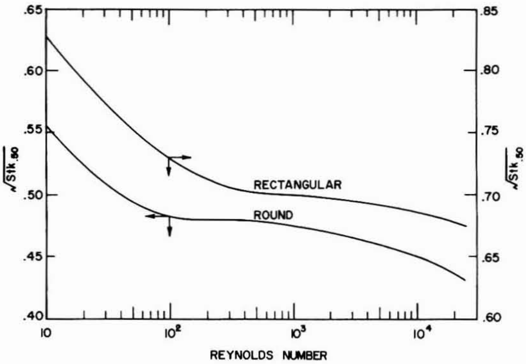


Figure 10. Effect of Reynolds number on 50% cut point of impactors

Rectangular impactor, S/W = 1 and T/W = 1; Round impactor, S/W = 0.5 and T/W = 1

The theoretical effect of jet Reynolds number on the impactor efficiency curve is shown in Figure 6b. The figure shows that the Reynolds number has a definite effect on the sharpness of cut of the efficiency curves at values below 500. However, as shown in Figure 10, the value of $St_{0.50}^{1/2}$ is relatively constant for Reynolds number values above about 100. Therefore, if sharp cut-off characteristics are not important, impactors can be operated below the recommended Reynolds number value of 500. In using the results of Figure 10 it should be noted that these curves are for S/W values of ½ and 1 for round and rectangular impactors, respectively. However, the curves should be relatively unchanged for S/W values larger than these values.

It is important to note in Figure 10 that varying the Reynolds number in the range below 100 may cause a significant change in the value of $St_{0.50}^{1/2}$. Thus, the usual procedure of calculating the cut-off particle diameter, D_{p2}, of an impactor stage at a new jet velocity, V_{o2}, from the value, D_{p1}, measured at a velocity, V_{o1}, using the equation

$$V_{o2}\rho_{p2}C_2D_{p2}^2 = V_{o1}\rho_{p1}C_1D_{p1}^2 \qquad (7)$$

may lead to substantial errors at low Reynolds numbers since the equation assumes that $St_{0.50}^{1/2}$ is independent of the jet velocity, or jet Reynolds number.

The "knee" near the lower end of the efficiency curve for Re = 25,000 shown in Figure 6b is similar to the one first observed by Davies and Aylward (1951), who had predicted the existence of the knee on the basis of potential flow theories. The knee appears to be the result of the very steep velocity gradient in the boundary layer around the stagnation point at high Reynolds numbers. This effect can also be seen in Figure 5b.

The theoretically predicted effect of the throat length on the efficiency curve shown in Figure 6c is seen to be small. However, as explained above, there is experimental evidence that in real rectangular impactors the influence of the throat length may be substantial when the flow is irregular.

Acknowledgment

We wish to thank the Numerical Analysis Center, University of Minnesota, for the use of the CDC 6600 digital computing facilities.

APPENDIX

Analytical Criteria for Determining Impaction of Particles

Analytical criteria can be developed for determining whether a particle will impact without following through the integration process until actual impaction has occurred.

Consider the equation of motion for the particle (Equation 4 in the text):

$$\frac{\mathrm{St}}{2}\frac{d^2y}{dt^2} = V_y - \frac{dy}{dt} \qquad \text{(A-1)}$$

If it is assumed that the fluid velocity in the y direction, V_y, would decrease linearly with distance from the value at the last grid line to zero at the plate, Equation A-1 becomes

$$\frac{d^2y}{dt^2} + \frac{2}{\mathrm{St}}\frac{dy}{dt} - \frac{2}{\mathrm{St}}\frac{V_1(\Delta + y_1 - y)}{\Delta} = 0 \qquad \text{(A-2)}$$

where V_1 is the fluid velocity in the y direction at the last grid line at a distance of y_1 from the impactor entrance, and Δ is the dimensionless distance (Δ'/W) from the last grid line to the plate. Equation A-2 is an ordinary differential equation of the second order with constant coefficients. The solution is:

$$y = c_1e^{m_1t} + c_2e^{m_2t} + (y_1 + \Delta) \qquad \text{(A-3)}$$

where

$$m_1 = -\frac{1}{\mathrm{St}} + \sqrt{\left(\frac{1}{\mathrm{St}}\right)^2 - \frac{2V_1}{\mathrm{St}\Delta}}$$

$$m_2 = -\frac{1}{\mathrm{St}} - \sqrt{\left(\frac{1}{\mathrm{St}}\right)^2 - \frac{2V_1}{\mathrm{St}\Delta}} \qquad \text{(A-4)}$$

The constants, c_1 and c_2, are determined from the initial conditions: $t = 0$, $y = y_1$, and $dy/dt = v_1$, where v_1 is the component of particle velocity in the y direction at the last grid line $y = y_1$. Using these initial conditions, we obtain

$$c_1 = \frac{m_2\Delta + v_1}{m_1 - m_2}$$

$$c_2 = \frac{-m_1\Delta - v_1}{m_1 - m_2} \qquad \text{(A-5)}$$

Equation A-3 will have one of three forms, depending on whether the quantity under the square root sign in Equation A-4 is negative, zero, or positive. These solutions are referred to as underdamped, critically damped, or overdamped, respectively, since the same equation and solution apply to a second-order mechanical or electrical system undergoing oscillation with damping.

For the underdamped case, which is obtained for large Stokes numbers, Equation A-3 can be written in the form

$$y = e^{pt}(A\cos qt + B\sin qt) + (y_1 + \Delta) \qquad \text{(A-6)}$$

where

$$p = -\frac{1}{\mathrm{St}}$$

$$q = \sqrt{\left|\left(\frac{1}{\mathrm{St}}\right)^2 - \frac{2V_1}{\mathrm{St}\Delta}\right|}$$

$$A = c_1 + c_2$$

$$B = i(c_1 - c_2)$$

The particle would always impact in this case, as one can see from the fact that $y = y_1 + \Delta$ when

$$A\cos qt + B\sin qt = 0 \qquad \text{(A-7)}$$

From Equation A-7, it can be determined that the particle would impact at a time

$$t = \frac{1}{q}\tan^{-1}\frac{q\Delta}{P\Delta + v_1} \qquad \text{(A-8)}$$

after it crosses the last grid line.

For the overdamped case, the particle will reach the impaction plate at $y = y_1 + \Delta$ when

$$c_1e^{m_1t} + c_2e^{m_2t} = 0 \qquad \text{(A-9)}$$

This condition would be satisfied if

$$t = \frac{\ln\left[\dfrac{m_1\Delta + v_1}{m_2\Delta + v_1}\right]}{m_1 - m_2} \qquad \text{(A-10)}$$

Here the particle would impact only if t is positive and finite.

Since Δ, V_1, St, and v_1 are all positive, m_1 and m_2 are negative. Further, $|m_2| > |m_1|$, so $m_1 - m_2$ is positive. Therefore, for t to be positive the condition

$$\frac{m_1\Delta + v_1}{m_2\Delta + v_1} > 1$$

must be satisfied. This can occur only when

$$v_1 > |m_2\Delta| \qquad \text{(A-11)}$$

Thus, Equation A-11 is a necessary and sufficient condition for the impaction of particles.

For the critically damped case, Equation A-11 also applies. However, in this case, $m_1 = m_2 = 1/\mathrm{St}$. Therefore, the criterion for the particle to impact is given by

$$v_1 > \Delta/\mathrm{St} \qquad \text{(A-12)}$$

Nomenclature

C = Cunnigham slip correction
D_p = Diameter of particle
E = impactor efficiency
m = mass of particle
q = fraction to total flow between the streamline of interest and the stagnation streamline along the impactor axis
Re = Reynolds number = $\rho V_o 2W/\mu$ for rectangular impactor = $\rho V_o W/\mu$ for round impactor
r', z' = cylindrical coordinates measured from centerline and entrance, respectively
r, z = dimensionless cylindrical coordinates, $r'/W, z'/W$
r_p = radius of particle
S = jet-to-plate distance
St = Stokes number = $\rho_p C V_o D_p^2/9\mu W$
St_c = critical Stokes number
$\mathrm{St}_{0.50}^{1/2}$ = value of $\mathrm{St}^{1/2}$ at 50% efficiency
T = throat length
t', t = time and dimensionless time $t'/W/V_o$
V_o = mean fluid velocity at throat
V_1', V_1 = fluid velocity and dimensionless fluid velocity (V'/V_o) at y_1'
V_x', V_y' = x and y components of fluid velocity
V_x, V_y = dimensionless components of fluid velocity $(V_x'/V_o$ and $V_y'/V_o)$
v_1', v_1 = particle velocity and dimensionless particle velocity (v_1'/V_o) at y_1'
W = jet width for rectangular impactor, = jet diameter for round impactor
x', y' = rectangular coordinates measured from centerline and entrance, respectively
x, y = dimensionless rectangular coordinates, x'/W, y'/W
X_c = distance of the hypodermic needle from the center of the variable point impactor

x_i = particle's point of impact (distance from center of impaction plate)

y_1', y_1 = vertical coordinate and dimensionless vertical coordinate of grid line adjacent to the impaction plate

Greek Letters

μ = fluid viscosity

ρ = fluid density

ρ_p = particle density

Δ', Δ = distance and dimensionless distance (Δ'/W) between the grid line adjacent to the impaction plate and the impaction plate

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Received for review September 24, 1973. Accepted February 14, 1974. Work supported in part under AEC Contract AT(11-1)-1248 and in part by an NSF traineeship.

Solubility of Higher-Molecular-Weight *n*-Paraffins in Distilled Water and Seawater

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■ The solubility of several *n*-paraffins has been determined in both distilled water and seawater. In all cases, the paraffins were less soluble in seawater than in distilled water. For example, the solubility of dodecane was 3.7 ppb in distilled water and 2.9 ppb in seawater. The corresponding values for hexacosane were 1.7 and 0.1 ppb. The magnitude of the salting out effect increased with increasing molar volume of the paraffins in accordance with the McDevit-Long theory. Calculations using the McDevit-Long theory gave values of salt coefficients in good agreement with those obtained experimentally. The salting out effect observed for the *n*-paraffins indicates the importance of estuaries in determining the geochemical transport and fate of *n*-paraffins as well as other organic molecules.

The solubility of normal paraffins from methane to decane (C_{10}) has been investigated by a number of workers (Claussen and Polglase, 1952; Morrison, 1952; McAuliffe, 1963, 1969). The most extensive work is that of McAuliffe (1963). He found that the log of the solubility decreases linearly with increasing number of carbon atoms. Franks (1966) and Baker (1959) found that the solubilities of normal paraffins heavier than decane are much higher than that which would be predicted by extrapolation of the linear relationship between log solubility and molar volume of the lower normal paraffins. Peake and Hodgson (1966, 1967) also extensively investigated the higher-molecular-weight normal paraffins. However, they were more concerned with investigation of the micellar properties of hydrocarbons, rather than determining thermodynamic solubilities. There is no mention in the literature of solubilities of the higher normal paraffins in high ionic strength media such as seawater.

Solubility studies on the *n*-paraffins in aqueous media of differing ionic strengths will be important in the study of the geochemical transport and fate of such molecules. Salting in or salting out processes may alter geochemical pathways as *n*-paraffins are transported through a salinity gradient, such as those in estuaries. Such studies will also have relevance to the subsurface transport and accumulation of crude oils. Increasing amounts of oil are entering the oceans as pollutants. This addition is estimated at 10 million tons/year (Blumer, 1971) and 100 million tons/year (SCEP, 1970). The major processes acting on oil after its introduction include dissolution, evaporation, microbial degradation, and chemical oxidation. This study focuses on the dissolution of several higher-molecular-weight *n*-paraffins from dodecane (C_{12}) to hexadecane (C_{26}) in both distilled water and seawater.

Experimental

Equilibration of hydrocarbons with water occurred in a closed flask environment. Erlenmeyer flasks (1000 ml) with ground glass stoppers were fitted with a horizontal side arm near the bottom. The side arm was equipped with a Teflon stopcock. In each case, 175 mg of hydrocarbon were equilibrated with 700 ml of water. Liquid hydrocarbons were added volumetrically by syringe. Solid hydrocarbons were weighed and added as such. The flasks

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Table I. Solubilities of Normal Paraffins in Seawater and Freshwater at 25°C

Molecule	Solubility in distilled water		Solubility in seawater		Solubility in distilled water from the literature mol frac × 10^{10}
	Mol frac × 10^{10}	Ppb	Mol frac × 10^{10}	Ppb	
Dodecane (C_{12})	4.0	3.7	3.1	2.9	8.9[a]
Tetradecane (C^{14})	2.0	2.2	1.5	1.7	6.3[a]
Hexadecane (C_{16})	0.7	0.9	0.3	0.4	5.0[a]
Octadecane (C_{18})	1.5	2.1	0.5	0.8	4.3[b]
Eicosane (C_{20})	1.1	1.9	0.5	0.8	
Hexacosane (C_{26})	0.8	1.7	0.06	0.1	

[a] Franks (1966). [b] Baker (1959).

were equilibrated by shaking gently on a constant temperature bath at 25 ± 0.1°C for 12 hr. After the flasks were shaken, they were allowed to sit in the shaking bath for 24 hr to allow dispersed droplets to rise to the surface.

Aliquots of 100 ml were removed through the side arm of the flask. Each sample was filtered with very gentle suction through a 0.45-μm Millipore filter to remove any small hydrocarbon droplets still in suspension. The following experiments were run to see if adsorption of dissolved hydrocarbons occurred upon the filters. A 100-ml aliquot of saturated hydrocarbon solution was filtered once. Another 100-ml aliquot from the same solution was filtered through one filter, and the filtrate was filtered again through a second filter. A third aliquot from the same solution was filtered sequentially through three filters in a similar fashion. Tests showed that for saturated solutions of dodecane (C_{12}), hexadecane (C_{16}), and eicosane (C_{20}), the final concentrations of filtered aliquots were the same regardless of the number of times they had been sequentially filtered. Thus adsorption of dissolved hydrocarbons upon the filters did not occur to any significant degree.

Each filtered aliquot was extracted three times with 10-ml portions of hexane. The first portion of hexane contained a normal paraffin internal standard which differed by only one or two carbon atoms from the hydrocarbon under investigation. Thus tridecane (C_{13}) was used as an internal standard for the solubility of tetradecane (C_{14}), while tetracosane (C_{24}) was the internal standard for hexacosane (C_{26}). The use of the internal standard ensured that any loss of the hydrocarbon under investigation, subsequent to filtering, could be compensated for. Each 30-ml hexane extract was evaporated to 0.1 ml under a stream of prepurified nitrogen gas.

The concentration of hydrocarbons was determined by injection of the concentrated hexane extract into a dual column gas chromatograph equipped with flame ionization detectors. The output was recorded by a strip chart recorder equipped with a mechanical integrator. Peak areas of the concentrated hexane extract were compared to peak areas of known concentration. The columns were two meters long by 2-mm inner diameter. The support phase was Chromosorb G (AW, DMCS), and the organic phase Dexsil 300. The columns were made in the fashion of Horning et al. (1963). The detectors were kept at 350°C and the inlet ports at 250°C. The oven temperature was variable depending upon the hydrocarbon being injected.

All fresh water was doubly distilled. Periodic blanks were run by extracting 100 ml of doubly distilled water. The natural seawater used in equilibration was taken at a depth of 25 meters to avoid possible contamination from surface slicks. The water was collected with a 30-liter Niskin bottle, and stored on board ship in 5-gal glass containers. The water was poisoned with a few ml of saturated mercuric chloride solution to avoid microbial activity. The seawater was filtered prior to use through a Gelman glass fiber filter. The salinity of the water was found to be 35 ± 0.5 parts per thousand as determined with a hand-held refractometer. Aliquots (100 ml) of seawater were extracted with hexane; the hexane was concentrated and injected into the gas chromatograph to see if levels of naturally existing hydrocarbons were high enough to preclude using natural seawater. Levels of naturally occurring *n*-paraffins in this seawater were found to be too low to cause any interference problems.

The biggest single source of contamination was trace hydrocarbons in the hexane. To avoid serious contamination, reagent grade hexane was doubly distilled, the second distillation being performed with a 60-cm long Vigreux column. The hexane was subsequently stored in amber bottles in the dark. Fresh hexane was distilled biweekly. All hydrocarbons were 99+% pure from Analabs Inc.

All glassware was rinsed with doubly distilled hexane to remove any contaminant hydrocarbons. The glassware was then soaked for 24 hr in a concentrated chromic acid bath, rinsed with doubly distilled water, and dried for 12 hr or more in an oven at 200°C. The glassware was not removed from the oven until just prior to use.

Results

The solubilities of the substances studies are shown in Table I, expressed as mole fractions and as ppb. Eight replications were made for each substance. The average of the deviations of the mean for each substance gave an experimental error of ±16%. The range of error is acceptable considering the amount of handling in preparation of a sample for measurement.

The discrepancies between the data presented here and literature values is thought to be due to the methods used for the removal of small hydrocarbon colloids. That such colloids exist is shown, for example, by values of 19.6 ppb and 13.4 ppb obtained for the "accommodation" of dodecane and hexadecane, respectively, in distilled water omitting the filtering step. Similarily Peake and Hodgson (1966, 1967) have shown that higher-molecular-weight *n*-paraffins may be accommodated as colloids up to 100 mg per liter. McAuliffe (1969) also demonstrated the existence of colloids for equilibrated solutions of undecane, tridecane, and tetradecane. It thus appears that removal of such colloids is a necessary step in determining solubilities. Franks (1966) did not filter or otherwise treat his samples for colloid removal. The techniques used by Baker (1959) were not specified.

Discussion

The solubilities of compounds in distilled water and

Table II. Salt Parameters for Normal Paraffins at 25°C

Paraffin	K_s, obsd	K_s, calcd
Dodecane	0.22	0.260
Tetradecane	0.25	0.298
Hexadecane	0.68	0.336
Octadecane	0.95	0.373
Eicosane	0.68	0.411
Hexacosane	2.23	0.521

higher ionic strength aqueous media may be related by the Setschenow equation,

$$\log_{10} S_o/S = KC_s \tag{1}$$

where S_o is the solubility in moles/liter in distilled water, S is the solubility in moles/liter in a salt solution of molarity C_s. As shown by Long and McDevit (1952), if the solubilities S_o, and S are small the empirical Setschenow parameter K, may be equated with the theoretical salt parameter, K_s. If the sign of K_s is positive, the solubility of a nonpolar compound will be less in salt solution than in fresh water solutions and salting out will occur. If K_s is negative the reverse is true and a nonpolar compound will be salted in. Values of K_s calculated for the various normal paraffins investigated in this work are shown in Table II. C_s is taken as 0.504 and is obtained in the manner described later in the text. Examination of Table II shows that K_s values for all paraffins are positive, and the magnitude of K_s increases from dodecane to hexacosane.

The McDevit and Long (1952) theory of salt effects attributes salting in or salting out to the effect of electrolytes upon the structure of water. They show that the work done by placing a molecule of molar volume V_l^0 in a salt solution is proportional to the degree of electrorestriction of the ions in the salt solution. K_s is given by the expression,

$$K_s = \frac{V_l^0(V_s - \bar{V}_s^0)}{2.3\, RT\beta_0} \tag{2}$$

where V_l^0 is the molar volume of pure hydrocarbon, V_s is the volume of "liquid" salt at temperature T, $\bar{V}_s^0$ is the partial molal volume of the salt at temperature T in distilled water, and β_0 is the compressibility of pure water. Frank and Evans (1945) and Némethy and Scheraga (1962) have shown that aliphatic hydrocarbons dissolve with an increase in "ice-likeness" in the structure of water surrounding the dissolved molecules. Ions for which $V_s - \bar{V}_s^0$ is positive disrupt this "ice-likeness" and salt out aliphatics, while ions for which $V_s - \bar{V}_s^0$ is negative enhance the "ice-likeness" and salt in aliphatics.

It is apparent from examination of Equation 2 that the only term which relates to the solute molecule is the molar volume term. Thus, under similar salt conditions, one would expect that salting in or salting out would increase as the molar volume of the solute increased. For the case of the normal paraffins, the salt effects on dodecane (V_l^0 = 228.7 ml/mol) should be less than the salt effects on hexacosane (V_l^0 = 456.5 ml/mol). Indeed this is what the experimentally observed values of K_s indicate.

By use of Equation 2, calculations were made to determine the magnitude and sign of K_s, and to compare them with observed values. Since seawater is a mixture of salts, the assumption is that the salt effects of each salt species upon the paraffins are additive. Gordon and Thorne (1967a,b) have found salt effects on naphthalene for a mixture of salts to be additive according to the equation

$$\log S = \log S^0 - \sum_{i=1}^{n} X_i K_{is} C_t \tag{3}$$

where X_i and K_{is} are the mole fraction and salting out parameter of the ith salt, and C_t is the sum of the individual salt molarities. This equation is assumed to hold for n-paraffins in seawater also. By comparing Equation 3 with Equation 1, it is apparent that the quantity, $\sum_{i=1}^{n} X_i K_{is}$ must be compared to experimental values of K_s. X_i and K_{is} have to be calculated for each salt species in seawater. For computational purposes, seawater is assumed to have the composition of the artificial seawater proposed by Lyman and Fleming (1940). Only the six most prevalent salts are used in the calculations. C_t is obtained by adding the moles of each salt species needed to give a salinity of 35.0 parts per thousand and converting from molality to molarity by multiplying by the density of the salt solution at 25°C (1.024 g/cm^3).

Values of the partial molal volume for the salts are taken from the review by Millero (1972). The volume of the "liquid" salt, or true nonhydrated volume of an ion in solution cannot be measured directly. Experimental estimates of the nonhydrated or intrinsic ion volume have been made from compressibility measurements (Gibson, 1934, 1935, 1938) and have been calculated (Hepler, 1957; Stokes and Robinson, 1957; Conway et al., 1965). These methods have indicated that the intrinsic volume of an ion in solution is about 77% larger than the crystal volume of an ion. However, Millero (1971) points out that this increase is caused by void space packing effects around the nonhydrated ion, and since the electrostatic pressure on the ion in water is similar to that on the ion in the crystal, the intrinsic volume of an ion in solution may be set equal to the volume of the ion in a crystal. Crystal volumes are given in the review by Millero (1971). Calculated results of K_s are shown in Table II for the normal paraffins. Calculated results thus show the same sign as experimental results, and are of the same magnitude.

The discrepancies between calculated and observed values for K_s are due primarily to uncertainties in the true values for V_s. In our calculations, we used minimum values for V_s. Also the value of the partial molal volume of the solute in solution (V_l^0) may be quite different than the molar volume of the pure liquid hydrocarbon.

It is interesting to consider some environmental implications of solubility measurements for the paraffins in freshwater and saltwater. Measurements of paraffin concentrations in various oceans have recently been made by Iliffe (1972), Parker et al. (1972), and Brown et al. (1973). Parker found that the concentrations of normal paraffins in various water samples from the Gulf of Mexico and Caribbean Sea ranged from 0.087 μg/l. to 1.1 μg/l. Iliffe found hydrocarbon concentrations (including branched paraffins and cycloparaffins) ranging from 5.4–18.2 μg/l. in the Gulf of Mexico and Caribbean Sea. Brown found concentrations of total saturated hydrocarbons in the Atlantic Ocean between 1.0 and 21.0 ppb. For the latter two workers, the weight fraction of reported hydrocarbon concentrations due to normal paraffins alone is not known. However, in comparing concentrations of hydrocarbons in ocean water with the solubility values of individual paraffins in seawater it seems that present hydrocarbon concentrations in ocean waters are not limited by their solubilities. Care must be taken, though, in extrapolating solubilities of individual hydrocarbons in seawater to seawater containing a large number of hydrocarbons, since it is unlikely that the solubilities of a number of hydrocarbons existing simultaneously in water are equal to the sum of the solubilities of the individual hydrocarbons.

Since our data indicate that normal paraffins are less soluble in seawater than in distilled water, it is possible to speculate upon the geochemical fate of dissolved normal paraffins entering the ocean from rivers. If the fresh river water is saturated or near saturated with respect to normal paraffins (because of pollution, for example), salting out will occur in the estuary. The salted out molecules might either adsorb on suspended minerals, on particulate organic matter, or rise to the surface to exist as surface slicks. In either event they will have a different biogeochemical pathway from that which they would have if they were dissolved.

The salting out of dissolved organic molecules in estuaries applies not only to normal paraffins but to all natural or pollutant organic molecules whose solubilities are decreased by addition of electrolytes. It is thus possible that regardless of the levels of dissolved organic pollutants in river water, only given amounts will enter the ocean in dissolved form owing to salting out effects of estuaries. Estuaries may act to limit the amount of dissolved organic carbon entering the ocean, but may increase the amount of particulate organic carbon entering the marine environment.

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Received for review June 15, 1973. Accepted February 20, 1974. This work was supported by National Science Foundation Grant GA-24235 and Grant GX-37351 from the NSF Office for the International Decade of Ocean exploration.

Oceanic Distribution of Low-Molecular-Weight Hydrocarbons

Baseline Measurements

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■ During the past seven years, 452 water samples from the open ocean and near shore have been analyzed to obtain data on the concentration and distribution of low-molecular-weight hydrocarbons in the marine environment. Average baseline concentrations in nanoliters per liter for these hydrocarbons in the open ocean are: methane, 49.5; ethane, 0.50; ethylene, 4.8; propane, 0.34; and propylene, 1.4. An empirical relationship, $\mathrm{CI} = \frac{1}{3}\,(C_1/C_1{}^* + C_2/C_2{}^* + C_3/C_3{}^*)$, referred to as the Contamination Index, is proposed to differentiate between open ocean clean water and water contaminated by hydrocarbons. C_1, C_2, and C_3 are concentrations of methane, ethane, and propane, respectively, while $C_1{}^*$, $C_2{}^*$, and $C_3{}^*$ are the average baseline concentrations of these hydrocarbons in clean ocean water. Water is considered to be uncontaminated if CI is not greater than 3, possibly contaminated if CI is greater than 3 but not greater than 5, and contaminated if CI is greater than 5.

There is a need to establish the baseline concentrations of low-molecular-weight hydrocarbons in the world ocean. This information will be useful in assessing the extent of oil pollution in the ocean environment. The purpose of this paper is to utilize all available data on low-molecular-weight hydrocarbons in surface ocean water to estimate the baseline concentrations for methane, ethane, ethylene, propane, propylene, and butanes in the world ocean. Since 1966, we have been obtaining data on the concentration and distribution of light hydrocarbons in the marine environment. The only reported measurements of light hydrocarbons in seawater are the data of Brooks and Sackett (*1*), Brooks et al. (*2*), and Lamontagne et al. (*3*). All the measurements of Brooks et al. are confined to the Gulf of Mexico and the western Caribbean. We have obtained measurements of light hydrocarbons in those same areas, and in the tropical North Atlantic, North Atlantic, Arctic, Mediterranean Sea, Black Sea, Red Sea, Arabian Sea, North Tropical Pacific, and South Pacific

Table I. Light Hydrocarbons in Surface Waters, Gulf of Mexico

Descriptive location, no. of samples (x) and date	Concentration units nanoliters/liter[a]							
	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	Iso and n-C_4H_{10}	CI[b] no.	Coordinates
1. Open Gulf (1) 6/73	37	0.11	6.4	0.05	1.6	Trace	0.4	22°58′N 86°13′W
2. Open Gulf (1) 6/71[c]	53	1.0	5.2	1.31	0.4	1.1	2.3	23°45′N 92°39′W
3. Open Gulf (1) 10/71[c]	79	1.1	1.7	0.70	0.1	0.60	2.0	27°30′N 87°08′W
4. Yucatan Shelf (1) 10/71[c]	57	Trace	3.8	0.90	0.1	0.40	1.3	21°03′N 86°52′W
5. Yucatan Shelf (1) 6/73	45	0.19	4.5	0.12	1.4	Trace	0.5	22°58′N 86°13′W
6. Yucatan Shelf (1) 6/73	34	0.20	6.5	0.24	1.2	Trace	0.6	21°41′N 36°34′W
7. Yucatan Shelf (1) 6/73	39	0.15	6.1	0.10	1.3	0.20	0.5	21°42′N 36°40′W
8. Yucatan Shelf (1) 6/73	32	0.12	6.8	0.10	1.7	0.60	0.4	22°25′N 87°08′W
9. Louisiana Shelf (1) 10/71[c]	550	9.5	5.3	1.8	3.8	1.2	12[d]	28°26′N 90°49′W
10. Louisiana Shelf (1) 10/71[c]	430	6.7	2.3	5.3	0.1	8.0	13[d]	28°25′N 91°23′W
11. Louisiana Shelf (1) 10/71[c]	6400	650[e]	—	240[f]	—	98	712[d]	28°25′N 91°36′W
12. Louisiana Shelf (1) 10/71[c]	1140	9.0	6.0	2.8	0.20	2.6	16[d]	28°29′N 92°13′W
13. Florida Shelf (1) 10/71[c]	113	1.2	5.3	1.0	0.10	1.1	2.5	18°52′N 83°58′W
14. Campeche Shelf (1) 10/71[c]	58	1.2	2.2	1.1	0.20	0.60	2.3	23°25′N 88°52′W
15. Mississippi R. Shelf (1) 10/66	68	4.5[e]	—	0.24	0.90	0.60	3.7	28°59′N 88°11′W
16. Mississippi R.—South Pass (1) 10/71[c]	2800	35[e]	—	65	16	30	106[d]	
17. Mississippi R. (1) 10/71[c]	2400	9.2[e]	—	820[f]	—	24	826[d]	
18. Mississippi R. Delta (1) 10/71[c]	8200	150	35.0	71	1.5	14	225[d]	
19. 5 miles of Freeport (1) 6/71[c]	210	1.9	15.0	0.70	0.40	0.2	3.4	28°48′N 95°13′W
20. 10 miles S. of Freeport (1) 6/71[c]	120	2.0	13.0	1.6	0.50	1.2	3.7	28°48′N 95°13′W
21. 15 miles of Freeport (1) 6/71[c]	120	2.0	13.0	1.2	0.40	0.60	3.3	28°48′N 95°13′W
22. 5 miles N. of Puerto Mexico (1) 6/71[c]	1130	240[e]	—	29	0.80	2.0	196[d]	18°25′N 94°25′W
23. 10 miles N. of Puerto Mexico (1) 6/71[c]	100	6.1	10.2	1.0	1.7	Trace	5.7[d]	18°25′N 94°25′W
24. 15 miles N. of Puerto Mexico (1) 6/71[c]	100	5.0	11.0	0.9	0.10	Trace	4.9	18°25′N 94°25′W
25. Texas Shelf (1) 10/71[c]	890	12	12	3.2	0.10	2.0	17[d]	28°53′N 93°44′W
26. Texas Shelf (1) 10/71[c]	380	1.4	4.6	2.0	0.10	2.7	5.5[d]	28°56′N 92°52′W
27. Texas Shelf (1) 10/71[c]	167	2.4	1.9	1.5	0.10	1.0	4.2	29°03′N 94°14′W

[a] Nanoliters of the hydrocarbon gas at STP dissolved in 1 liter of water. One nanoliter = 10^{-6} ml. [b] CI = $\frac{1}{3}(C_1/C_1^* + C_2/C_2^* + C_3/C_3^*)$ where CI is the Contamination Index number; C_1, C_2, and C_3 are concentrations of methane, ethane, and propane, respectively, C_1^*, C_2^*, and C_3^* are the average baseline concentrations for clean ocean water; 427 samples used to establish baseline concentrations. [c] Samples collected in collaboration with Brook's et al. See references. [d] Contaminated samples based on CI number. [e] Ethane concentration masks ethylene concentration. [f] Propane concentration masks propylene concentration. [g] Samples collected in collaboration with Dr. J. Bunt, Univ. of Miami. [h] Samples collected in collaboration with W. D. Smith, NRL.

Table II. Light Hydrocarbons in Surface Waters, Caribbean Sea

Descriptive location, no. of samples (x) and date	Concentration units nanoliters/liter[a]							
	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	Iso and n-C_4H_{10}	CI[b] no.	Coordinates
28. Antilles Isls. (1) 5/71	40	0.25	4.1	0.11	1.3	Trace	0.5	16°38′N 62°32′W
29. Antilles Isls. (1) 5/71	44	0.12	4.1	0.10	1.3	Trace	0.5	16°03′N 62°21′W
30. Antilles Isls. (1) 5/71	49	0.20	5.1	0.10	1.2	Trace	0.6	15°03′N 61°51′W
31. Antilles Isls. (1) 5/71	43	0.20	4.0	0.08	1.2	Trace	0.5	14°27′N 61°37′W
32. Antilles Isls. (1) 5/71	40	0.15	2.9	0.06	0.9	Trace	0.4	13°54′N 61°12′W
33. Northern Antilles Isls. (1) 5/71	42	0.16	4.6	0.10	1.3	Trace	0.5	17°46′N 63°10′W
34. Northern Antilles Isls. (1) 5/71	42	0.25	4.1	0.10	1.3	Trace	0.5	17°11′N 62°55′W
35. Cariaco Trench (10) 5/71	62	0.31	6.0	0.20	1.1	Trace	0.8	10°38′N 65°55′W
36. North of Cariaco Trench (1) 5/71	42	0.22	3.8	0.11	1.0	Trace	0.5	10°40′N 65°40′W
37. Cariaco Trench (2) 4/69	51	Trace	2.4	0.06	0.6	Trace	0.4	16°38′N 64°44′W
38. Grenada Banks (6) 5/71	58	Trace	2.2	Trace	0.5	Trace	0.4	11°33′N 61°53′W
39. Windward Passage (1) 7/73	41	0.22	12.0	0.12	2.3	Trace	0.5	21°45′N 72°40′W
40. Mid. Caribbean (1) 5/70	43	0.40	7.8	0.10	1.2	Trace	0.7	12°19′N 78°38′W
41. Mid. Caribbean (3) 5/70	43	Trace	7.4	Trace	1.1	Trace	0.3	13°48′N 77°50′W
42. South of Jamaica (1) 5/70	45	Trace	8.4	1.0	5.8	Trace	1.3	17°12′N 75°32′W
43. Northern Caribbean (2) 7/73	39	0.20	7.3	0.20	1.9	0.14	0.6	19°09′N 70°55′W
44. Northern Caribbean (1) 7/73	37	0.22	9.2	0.06	1.7	Trace	0.5	19°02′N 78°30′W
45. Northern Caribbean (1) 7/73	39	0.22	12.0	0.07	2.5	Trace	0.5	19°30′N 75°30′W
46. Mysterosa Bank (1) 10/71[c]	56	Trace	3.8	0.80	0.2	1.0	1.2	18°52′N 83°58′W
47. Near Eastern Cuba (1) 7/73	42	0.22	12.0	0.14	2.5	Trace	0.6	20°06′N 73°42′W
48. Bartlett Deep (1) 7/73	37	0.16	5.2	0.10	1.6	Trace	0.5	18°54′N 80°26′W
49. N.W. Caribbean (1) 7/73	32	0.14	6.6	0.08	1.3	Trace	0.4	20°13′N 85°36′W

See Table I for footnotes.

from the equator to the Antarctic. Other areas investigated are: the Potomac and York Rivers; Chesapeake Bay; near shore in Miami; several regions of anoxic water, such as Lake Nitinat, Cariaco Trench, Black Sea; and a hot brine of the Red Sea. Ocean areas yet to be surveyed are the Indian Ocean, the South Atlantic, and the North Pacific above Hawaii. The accumulated results for light hydrocarbons will be used to discuss the distribution of these compounds in the surface waters of the world ocean. An empirically derived Contamination Index is utilized to identify polluted waters.

Analytical Procedures

Most of the hydrocarbon measurements were made by gas chromatography aboard ship. In this technique, the dissolved hydrocarbons are first stripped from solution by purging with helium, and are then concentrated in cold traps containing appropriate adsorbents; they are subsequently released by an increase in temperature and swept into the gas chromatograph by a second stream of helium carrier gas. With this method, sample size is not restricted, and very dilute solutions may be analyzed.

Two cold traps at −77°C were used in series. In the first, activated alumina was used to trap all hydrocarbons except methane; in the second, a mixture of activated charcoal and molecular sieve was used to trap methane. When the stripping was complete, the traps were isolated by closure of appropriate valves, and their temperature was raised to approximately 90°C. Helium carrier gas was then used to strip each adsorbent, in turn, of the adsorbed

Table III. Light Hydrocarbons in Surface Waters, Atlantic Ocean

	Concentration units nanoliters/liter[a]							
Descriptive location, no. of samples (x) and date	**CH_4**	**C_2H_6**	**C_2H_4**	**C_3H_8**	**C_3H_6**	**Iso and n-C_4H_{10}**	**Cl[b] no.**	**Coordinates**
50. Lower Sargasso Sea (5) 5/71	44	0.30	6.8	0.10	2.0	Trace	0.6	30°14′N 70°09′W
51. Transit-Sargasso to Trinidad (6) 5/71	40	0.20	6.4	0.09	2.0	Trace	0.5	26°43′N 68°03′W
52. Transit-Sargasso to Trinidad (7) 5/71	38	0.13	6.5	0.06	1.5	Trace	0.4	22°49′N 66°47′W
53. Transit-Sargasso to Trinidad (5) 5/71	39	0.12	5.1	0.07	1.3	Trace	0.4	18°22′N 63°24′W
54. East of Trinidad (4) 5/71	38	0.26	2.7	0.18	1.3	Trace	0.6	11°28′N 60°29′W
55. Transit-Bermuda to Norfolk (1) 12/69	65	Trace	11.0	Trace	0.6	Trace	0.4	32°14′N 64°37′W
56. Transit-Bermuda to Norfolk (1) 12/69	46	Trace	3.5	Trace	0.3	Trace	0.3	35°12′N 67°53′W
57. E. of Norfolk, Va.-Shelf (1) 12/69	280	1.0	3.3	0.10	0.3	Trace	2.7	36°36′N 74°41′W
58. Trinidad Shelf (2) 5/71	108	0.40	2.7	0.10	0.9	Trace	1.1	11°28′N 60°22′W
59. N. of Lesser Antilles Isls. (1) 4/69	36	Trace	3.4	Trace	0.7	Trace	0.2	17°50′N 61°30′W
60. N. of Lesser Antilles Isls. (2) 4/69	57	Trace	2.4	Trace	0.8	Trace	0.4	16°50′N 60°54′W
61. E. of Lesser Antilles Isls. (1) 4/69	42	Trace	2.3	Trace	0.5	Trace	0.3	16°08′N 60°26′W
62. E. of Lesser Antilles Isls. (1) 4/69	40	Trace	2.1	Trace	0.6	0.05	0.3	15°21′N 59°55′W
63. Near Barbados (1) 4/69	31	Trace	2.4	Trace	0.6	Trace	0.2	13°13′N 59°07′W
64. R. of Trinidad (1) 4/69	33	Trace	1.1	Trace	0.4	Trace	0.2	10°38′N 60°05′W
65. E. of Trinidad (1) 4/69	39	Trace	0.7	Trace	Trace	Trace	0.3	10°38′N 60°05′W
66. E. of Trinidad (8) 4/69	36	Trace	1.8	Trace	Trace	Trace	0.2	10°38′N 60°05′W
67. Mid Atlantic (1) 5/66	40	Trace	9.9	0.20	0.6	Trace	0.5	52°35′N 20°09′W
68. E. of North Carolina Coast (1) 6/68	37	1.0	3.7	Trace	0.5	Trace	0.9	33°40′N 74°47′W
69. E. of South Carolina Coast (1) 6/68	37	1.1	3.6	0.10	0.4	Trace	1.1	32°58′N 74°52′W
70. E. of Northern Florida (1) 6/68	62	1.0	6.8	0.10	0.9	Trace	1.2	30°08′N 75°18′W
71. E. of Southern Florida (1) 6/68	34	1.1	3.0	Trace	0.8	Trace	1.0	26°35′N 74°43′W
72. Gulf Stream-Miami (10) 1972[g]	59	0.60	6.0	0.70	1.5	0.80	1.5	Jan thru June
73. E. of Bahaman Islands (4) 7/73	36	0.21	6.9	0.08	2.2	0.05	0.5	25°20′N 75°11′W
74. Exuma Sound (1) 6/68	45	1.0	3.8	0.10	1.0	Trace	1.1	24°00′N 75°30′W
75. Grand Caicos Isl. (1) 6/68	48	1.0	3.0	Trace	0.8	Trace	1.0	22°04′N 71°43′W
76. Exuma Sound (3) 7/73	39	0.40	7.7	0.09	2.3	Trace	0.6	24°33′N 76°14′W
77. Miami-Nearshore (10) 1972[g]	190	1.5	16.0	0.94	4.7	2.20	3.2	Jan thru June
78. Miami-Nearshore (9) 6/72[g]	280	1.4	26.0	1.20	4.8	4.40	4.0	24-hr sampling period
79. Miami-Dockside (4) 1972[g]	1,300	2.6	30.0	2.8	11.0	4.70	13[d]	Jan thru June
80. N.E. of Windward Passage (1) 7/73	39	0.21	10.0	0.16	2.2	Trace	0.6	21°58′N 72°52′W
81. S.E. of Chesapeake Bay Entrance (1) 6/68	96	1.5	7.2	0.50	2.9	Trace	2.1	36°30′N 75°43′W
Norwegian-Greenland Sea Transit—Noon Positions—Av of Daily Samples								
82. Nearshore Scotland (7) 8/4/71[h]	62	1.0	5.0	1.0	0.9	Trace	2.1	58°28′N 5°41′W
83. Transit (7) 8/5/71[h]	63	1.4	3.4	0.9	1.3	Trace	2.2	63°18′N 3°28′W
84. Transit (7) 8/6/71[h]	58	1.3	2.8	1.3	1.1	Trace	2.5	66°30′N 1°35′W
85. Transit (7) 8/7/71[h]	62	1.4	2.4	1.3	0.8	Trace	2.6	70°11′N 1°11′W
86. Transit (7) 8/8/71[h]	69	1.2	2.1	1.4	1.0	Trace	2.6	72°59′N 2°58′E
87. Transit (7) 8/9/71[h]	64	1.2	1.7	1.4	0.6	Trace	2.6	76°24′N 6°00′E
88. Transit (5) 8/10/71[h]	65	1.3	1.7	0.7	0.6	Trace	2.0	77°22′N 9°50′E
89. Greenland Ice Pack (8) 8/13/71[h]	78	1.7	3.6	0.6	1.9	Trace	2.2	77°52′N 1°38′W
90. Greenland Ice Pack (8) 8/14/71[h]	77	1.6	3.3	0.71	1.6	Trace	2.3	77°54′N 2°00′W
91. Greenland Ice Pack (8) 8/15/71[h]	103	1.9	4.2	1.1	1.9	Trace	3.0	77°57′N 4°55′W
92. Greenland Ice Pack (8) 8/16/71[h]	72	1.6	3.2	0.73	1.3	Trace	2.3	77°30′N 1°55′W
93. Transit (8) 8/17/71[h]	66	1.2	2.7	0.50	0.6	Trace	1.7	77°26′N 0°59′W
94. Transit (8) 8/18/71[h]	68	1.3	2.5	0.40	0.8	Trace	1.7	73°31′N 8°19′E

See Table I for footnotes.

Table IV. Light Hydrocarbons in Surface Waters, Pacific Ocean

	Concentration units nanoliters/liter[a]							
Descriptive location, no. of samples (x) and date	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	Iso and n-C_4H_{10}	Cl[b] no.	Coordinates
95. S.W. of Panama (4) 5/29/71	69	0.2	8.0	0.18	1.4	Trace	0.8	8°12′N 79°38′W
96. Transit (2) 5/30/71	53	0.2	10	0.15	1.9	Trace	0.6	8°13′N 84°45′W
97. Transit (6) 5/31/71	56	0.31	11	0.6	3.6	Trace	1.2	9°48′N 90°22′W
98. Transit (6) 6/1/71	51	0.2	9.5	0.2	2.1	Trace	0.7	12°12′N 96°38′W
99. Transit (6) 6/2/71	48	0.2	9.0	0.2	2.1	Trace	0.7	14°10′N 103°34′W
100. Transit (6) 6/3/71	47	0.1	6.7	0.1	1.4	Trace	0.5	16°03′N 110°21′W
101. Transit (7) 6/4/71	46	0.2	7.1	0.1	1.1	Trace	0.5	17°29′N 116°00′W
102. Transit (3) 6/5/71	44	0.3	4.9	0.1	0.9	Trace	0.6	16°00′N 120°29′W
103. Transit (6) 6/6/71	50	0.2	5.7	0.1	0.7	Trace	0.6	19°00′N 126°54′W
104. Transit (6) 6/7/71	49	0.2	5.9	0.1	0.7	Trace	0.6	20°20′N 134°03′W
105. Transit (6) 6/8/71	47	0.21	4.5	0.1	0.9	Trace	0.6	21°02′N 139°57′W
106. Transit (5) 6/9/71	44	0.1	4.2	0.1	0.6	Trace	0.5	21°22′N 146°14′W
107. Hawaiian Isls. (3) 6/10/71	44	0.1	4.0	0.1	0.6	Trace	0.5	21°22′N 151°48′W
Long Beach, Calif.—Antarctica Transit—Noon Positions—Av of Daily Samples								
108. Transit (1) 11/18/72	42	0.15	2.3	0.10	0.65	0.3	0.5	21°00′N 129°00′W
109. Transit (5) 11/19/72	43	0.29	2.2	0.27	1.5	0.2	0.7	17°21′N 131°31′W
110. Transit (4) 11/20/72	42	0.28	2.7	0.28	1.5	0.14	0.7	13°10′N 134°10′W
111. Transit (5) 11/21/72	41	0.25	3.9	0.33	2.6	0.3	0.8	8°42′N 137°09′W
112. Transit (4) 11/22/72	42	0.28	5.2	0.37	3.3	1.3	0.8	4°23′N 139°20′W
113. Transit (3) 11/23/72	42	0.31	5.7	0.32	2.2	0.2	0.8	0°00′N 142°03′W
114. Transit (7) 11/24/72	41	0.25	4.5	0.32	2.9	0.1	0.8	4°36′S 143°40′W
115. Transit (7) 11/25/70	42	0.29	5.3	0.42	3.4	0.2	0.9	9°20′S 145°51′W
116. Tahiti (5) 11/26/72	41	0.22	3.2	0.37	2.5	0.3	0.8	14°00′S 147°59′W
117. Transit (6) 11/29/72	41	0.23	3.5	0.33	2.3	0.1	0.8	16°38′S 148°44′W
118. Transit (5) 11/30/72	40	0.19	2.7	0.22	1.7	Trace	0.6	19°21′S 153°01′W
119. Transit (7) 12/1/72	41	0.17	2.5	0.17	1.6	Trace	0.6	24°54′S 157°11′W
120. Transit (7) 12/2/72	44	0.14	2.7	0.14	1.8	Trace	0.5	28°34′S 161°32′W
121. Transit (5) 12/3/72	45	0.15	3.1	0.12	1.6	Trace	0.5	31°55′S 165°59′W
122. Transit (4) 12/4/72	49	0.23	2.9	0.15	1.4	Trace	0.6	34°32′S 170°14′W
123. Transit (6) 12/5/72	51	0.32	4.6	0.25	2.4	Trace	0.8	37°56′S 175°55′W
124. Transit (4) 12/6/72	51	0.23	2.6	0.22	1.3	Trace	0.7	40°32′S 178°28′W
125. New Zealand (5) 12/15/72	74	0.47	3.8	0.36	1.2	Trace	1.2	41°31′S 174°49′E
126. Transit (3) 12/16/72	57	0.33	4.3	0.29	1.6	Trace	0.9	46°44′S 174°49′E
127. Transit (4) 12/17/72	57	0.21	3.1	0.16	0.9	Trace	0.7	52°28′S 175°49′E
128. Transit (7) 12/18/72	59	0.27	3.6	0.32	1.1	Trace	0.9	56°44′S 178°18′E
129. Transit (7) 12/19/72	68	0.43	3.2	0.55	1.4	Trace	1.3	62°05′S 177°30′E
130. Transit-Ice (3) 12/20/72	59	0.31	2.6	0.28	0.9	Trace	0.9	66°50′S 177°04′E
131. Transit-Ice (3) 12/21/72	47	0.45	2.0	0.40	1.1	Trace	1.0	70°23′S 175°35′E
132. Transit-Ice (1) 12/22/72	64	0.68	5.8	0.57	1.4	0.5	1.4	73°55′S 173°20′E
133. Ross Ice Shelf (1) 12/23/72	67	2.0	9.5	1.3	3.3	0.2	3.1	77°10′S 173°25′E

See Table I for footnotes.

Table V. Light Hydrocarbons in Surface Waters, Miscellaneous Samples

	Concentration units nanoliters/liter[h]							
Descriptive location, no. of samples (x) and date	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	Iso and n-C_4H_{10}	Cl[a] no.	Coordinates
134. Lake Nitinat (1) 11/67	850	0.3	4.8	0.3	3.2	0.3	6.2[d]	Lake Nitinat
135. Arabian Sea (1) 6/67	52	0.3	4.3	0.2	1.6	—	0.7	18°42′N 65°12′E
136. Mediterranean Sea (1) 5/67	53	0.5	3.0	0.4	1.2	—	1.1	36°30′N 13°45′E
137. E. Mediterranean Sea (1) 5/67	50	0.4	4.6	0.2	1.9	—	0.8	32°52′N 30°48′E
138. Red Sea (1) 6/67	47	0.5	4.3	0.2	1.9	—	0.8	21°24′N 38°07′E
139. Sargasso Sea (1) 9/67	55	0.6	6.0	0.13	0.8	—	0.9	31°55′N 64°08′W
140. Black Sea (1) 5/67	80	1.1	7.0	0.2	3.1	—	1.5	42°46′N 30°16′E
141. York River, Va. (6) 11/71	850	610	13.0	1100	8.0	220	1491[d]	Tidal Influence
142. Potomac River-Wilson Bridge (1) 6/68	3,800	4.9	11.0	2.1	6.8	1.5	31	Tidal Influence
143. Lower Chesapeake Bay (3) 6/68	750	7.3	9.0	1.3	2.9	0.8	11	37°28′N 76°08′W

See Table I for footnotes.

gases, and to carry these gases into the chromatograph for further separation and analysis. A four-foot column containing activated alumina with 10% Nujol was used to separate low-molecular-weight hydrocarbons other than methane. Methane was separated on a molecular sieve column. A schematic diagram of the apparatus is presented elsewhere by Swinnerton and Linnenbom, (*4*).

For the light hydrocarbons, the absolute sensitivity of the method is approximately 2×10^{-12} mol. On the basis of 1-liter water samples, this sensitivity coresponds to 5×10^{-8} ml of dissolved gas at standard temperature and pressure (STP) per liter of seawater. At this lower limit, the precision of the method, on the basis of replicate measurements under laboratory conditions, is ±10%. For quantities of gas greater by a factor of 10 or more, the precision improves to ±1.0%. Additional error incurred during field operations may increase this spread in uncertainty. The chromatograph was calibrated with an artificial gas mixture containing known amounts of the hydrocarbons in question.

Results

All of the results for low-molecular-weight hydrocarbons in the surface seawater are listed in Tables I–V. Figure 1 is a map of the world showing the locations where the samples were taken. Sample numbers in Figure 1 correspond to those in Tables I–V. A total of 452 samples were collected over a seven-year period. In each table, column 1 gives the descriptive location, number of samples (x), and date of collection. Columns 2–7 present the various low-molecular-weight hydrocarbon concentrations in nl liter^{-1} (nanoliters of the hydrocarbon gas at STP per liter of water). Column 8 is the Contamination Index (explained below), and column 9 lists the coordinates of each sample.

Discussion

All of the data presented in the Tables I–V concern concentrations of light hydrocarbons in surface waters. Several general observations can be made. Surface concentrations appear to be consistent from area to area. Methane in seawater has about the value one would expect on the basis of its partial pressure in the atmosphere. For the C_2–C_4 hydrocarbons, atmospheric partial pressure data are just now becoming available (*5, 6*).

In the upper layers of the oceans from 0–150 meters, we have found pronounced concentration peaks, with the olefins generally being higher in concentration than their saturated homologs (Figures 2 and 3). This nonhomogeneous distribution suggests the existence of processes occurring at rates faster than physical mixing rates. Plankton distributions in the upper layer also show pronounced peaks, which suggests a possible correlation between the hydro-

Figure 1. Transits and individual stations

(1–27) Gulf of Mexico, (28–49) Caribbean Sea, (50–81) Tropical N. Atlantic, (82–94) Norwegian Sea and Arctic Ocean, (95–107) Tropical N. Pacific, (108–133) Long Beach, Calif., to Antarctic via New Zealand, (134) Lake Nitinat (135) Arabian Sea), (136–137) Mediterranean Sea, (138) Red Sea, (140) Black Sea, (141–143) Chesapeake Bay and Potomac River

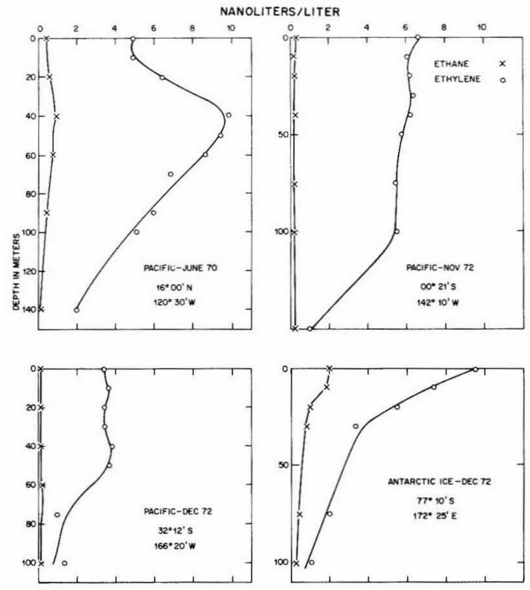

Figure 2. Vertical distribution of ethane (x) and ethylene (o) in the North and South Pacific Ocean and the Antarctic Ocean

Concentration units are nanoliters/liter, depth in meters

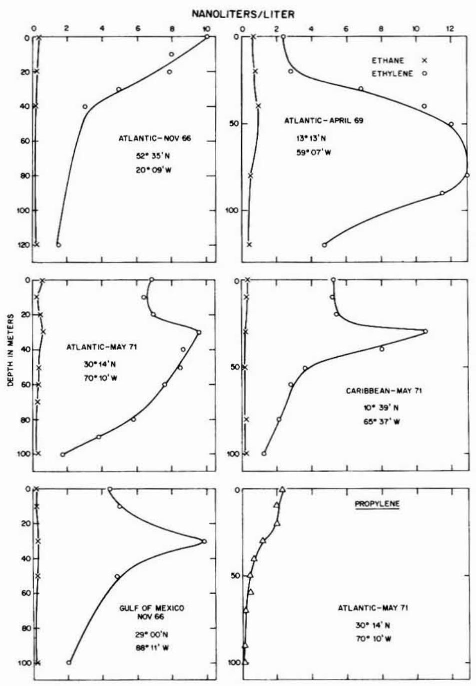

Figure 3. Vertical distribution of ethane (×), ethylene (O), and propylene (Δ) in the North Atlantic, Gulf of Mexico, and Caribbean Sea

Concentration units are nanoliters/liter, depth in meters

carbon distribution and biological processes. Laboratory experiments involving marine organisms have shown substantial production of unsaturated hydrocarbons, such as ethylene and propylene, and only minimal, if any, increase in the concentrations of ethane and propane (*7*).

In oxygenated waters, concentrations of saturated light hydrocarbons generally tend to decrease with increasing depth, but in anoxic areas the situation is reversed, with methane increasing three to four orders of magnitude, and ethane approximately one to two orders of magnitude. Unsaturated compounds, however, appear only as traces in truly anoxic environments. This suggests that the mechanism for hydrocarbon production in anoxic waters is different from that in oxygenated upper layers. It is known that methane is produced by anaerobic decomposition of organic matter, and this may also be true for higher-molecular-weight hydrocarbons.

Contaminated Water. For the purpose of this paper, the criterion for distinguishing contaminated water will be based on the concentrations of methane, ethane, and propane. As a first approximation, it will be assumed that a methane concentration of 90 nl liter^{-1} constitutes an upper limit for uncontaminated water. This concentration was obtained by multiplying the solubility coefficient for methane in fresh water at 0°C by the average atmospheric partial pressure of methane, which is 1.5 ppm. It is then obvious that methane concentrations in samples 9–12 and 16–18, for example, are well above 90 nl liter^{-1} and that these samples are contaminated. It is not surprising that waters of the Louisiana Shelf and Mississippi Delta are found to be high in methane. Several factors could be responsible: organic decay, the result of anaerobic conditions, gas and oil seeps from oil well rigs, and man-made sources, such as shipping activity.

Contamination Index. A second, more definitive approximation can be made by using an empirical formula, $CI = \frac{1}{3}(C_1/C_1^* + C_2/C_2^* + C_3/C_3^*)$, which we call the Contamination Index (column 8, Tables I–V). This formula can be used to differentiate between clean and contaminated seawater. C_1 refers to the methane concentration, while C_2 and C_3 refer to ethane and propane concentrations. C_1^*, C_2^*, and C_3^* are average baseline concentrations based on the analysis of 427 clean ocean water samples, where $C_1^* = 49.5$ nl liter^{-1}; $C_2^* = 0.50$ nl liter^{-1}; and $C_3^* = 0.34$ nl liter^{-1}. Ethane and propane concentrations are utilized because these gases are always present in anoxic water environments, and are also commonly found in gas and oil seeps, which occur both on land and in the ocean. They are good indicators of contaminated water systems (*1*). The concentration ranges of the gases in nl liter^{-1} in clean open ocean water are 31–80 for methane, 0.1–1.7 for ethane, and 0.05–1.4 for propane. Undoubtedly these ranges are due in part to the effect of temperature on gas solubility (the highest concentrations are found at high latitudes). When reliable values of the solubility coefficients of these gases in seawater as functions of temperature become available, it will be possible to take into account temperature effects in the determination of baseline values.

The high levels of ethane and propane in the Norwegian Sea (samples 82–94) may be due in part to an outflow of the North Sea into the Norwegian Sea. There are considerable oil and gas reserves under the North Sea, many of which are being exploited. There are no available data on the concentrations of methane and propane in the North Sea's outflow.

To establish a numerical basis for distinguishing between clean and contaminated water, the highest known concentrations of methane, ethane, and propane in clean open ocean water, as indicated above, were utilized to calculate a criterion Contamination Index. The criterion Contamination Index calculated from these values is 3.0.

Therefore, all Contamination Index values not greater than three are considered to indicate clean water environments. A transition range in which CI is greater than three but not greater than five is arbitrarily chosen to provide for questionable samples. A sample with CI above five would be considered contaminated. In Tables I–V, the range of ethane concentration in contaminated samples is 1.4 to 650 nl liter^{-1}, and the average concentration is 71 nl liter^{-1}. The corresponding concentration range for propane is 1.0 to 1100 nl liter^{-1}, with an average of 95 nl liter^{-1}. All contaminated samples reported in Tables I–V are designated by a superscript *d*.

It is noteworthy that most of the open ocean samples have CI values less than unity. The reason is that most of these samples were collected in tropical and subtropical areas, whereas the baseline averages (denominators in the CI formula) are biased upward by the contributions from high latitudes.

Unsaturated C_2 and C_3 Hydrocarbons. Ethylene and propylene concentrations are not used to calculate the Contamination Index, because they are found in relatively high concentrations in both the open ocean and near shore contaminated water. They can, however, be used as a guideline to productivity (*2, 7, 8*). Baseline concentrations of ethylene in the open ocean range from 0.7–12.1 nl liter^{-1}, with an average of 4.8. In water that has a Contamination Index greater than five, the range of ethylene concentration is 1.9–35 nl liter^{-1}, with an average of 11.0.

Propylene concentrations in open ocean water range between 0.1 and 5.8 nl liter^{-1}, with an average of 1.4. The range of propylene concentration in contaminated water is 0.1–16 nl l^{-1}, with an average of 2.8. In general, the concentrations of ethylene and propylene decrease with increasing depth in the water column, reaching trace levels at 150–200 meters (Figures 2 and 3). Production of the unsaturated compounds seems to be related to biological processes and/or photochemical reactions on organic matter in the seawater. It is then not unexpected that the production of unsaturated hydrocarbons in near shore areas is equal to or higher than in the open ocean, as there can be considerably higher concentration of organic matter in the near shore areas. In a truly anoxic environment such as the Cariaco Trench, the unsaturated hydrocarbon concentrations decrease rapidly to trace levels.

C_4 Hydrocarbons. In general, the iso- and normal butanes are in relatively low concentration, usually in trace amounts (about 0.05 nl l^{-1}) in the open ocean samples. Measurable concentrations of butanes are observed in the near shore contaminated areas, as indicated by samples 11–18. Butane concentrations also increase very rapidly in truly anoxic environments. Butenes appear to behave similarly to ethylene and propylene in both distribution and concentration range. They are not reported in the tables, because only a few samples have been measured.

Summary of Baseline Data. The surface waters of the open ocean have relatively low concentrations of saturated light hydrocarbons. Methane in the surface waters of the open ocean is nearly in equilibrium with the atmosphere, while at nearshore areas, the methane concentration may be over 100-fold higher. The average concentration of methane in open ocean surface water is determined to be 49.5 nl liter^{-1}. This average is closer to typical values for tropical water masses, primarily because more samples have been obtained from these areas. Methane concentrations in samples, for which the Contamination Index is greater than five, range from 103–3800 nl liter^{-1}, with an average value of 1250. Baseline concentrations for ethane and propane in the open ocean average 0.50 nl liter^{-1} and 0.34 nl liter^{-1}, respectively. Contaminated nearshore samples usually contain 100–200 times the baseline concentrations of ethane and propane. Baseline concentrations of ethylene and propylene average 4.8 and 1.4 nl liter^{-1}, respectively, and the concentrations of these two olefins appear to be influenced by biological activity and productivity, rather than by contamination.

To demonstrate the usefulness of methane, ethane, and propane for determining the degree of contamination, one needs only to compare the ratios of open ocean concentrations with the contaminated concentrations. Using average calculated concentrations from each of the above, the following ratios (contaminated/open ocean) can be determined: methane, $1250/49.5 = 25$; ethane, $71/0.50 = 142$; propane, $95/0.34 = 280$; ethylene, $11.0/4.8 = 2.3$; propylene, $2.8/1.4 = 2$. It is obvious from these calculations that the saturated low-molecular-weight hydrocarbons can serve as sensitive indicators for detecting the presence of man-made or natural hydrocarbon pollutants. Unsaturated low-molecular-weight hydrocarbons as indicators of contamination or pollution do not appear to be as sensitive, as there is only a factor of two difference between contaminated and open ocean samples.

Acknowledgment

We thank Peter E. Wilkniss and C. H. Cheek for their critical evaluation of this manuscript.

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Received for review November 23, 1973. Accepted March 13, 1974.

Bacterial Degradation and Emulsification of No. 6 Fuel Oil

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■ The bacterial cultures were isolated from sewage which removed almost completely the paraffinic components from Grade 6 fuel oil (Bunker C oil). Of the major components in fuel oil, only the saturate fraction decreases during biodegradation. These microbes, particularly culture B2, produce a very active emulsifying agent for Grade 6 fuel oil. This emulsifier is synthesized from the paraffinic components in the fuel oil. Oil globules are 3–16μ size. This emulsifier appears to be a high-molecular-weight polysaccharide. Low temperatures and high salt levels tend to inhibit the emulsification process, although emulsification does occur. Thus it would appear that the major emulsification process involved in a massive oil spill is attributed to microbial emulsification.

Surface water oil spillage treatment was recently enhanced by taking into consideration the potential oil degradability by microorganisms. The authors (Zajic and Supplisson, 1972) showed that biodegradation and dispersion of No. 6 fuel oil, also referred to as "Bunker C," was readily achieved with a mixed microbial population containing bacteria and fungi.

Iguchi et al. (1969), Suzuki et al. (1969), and Hisatsuka et al. (1971) reported that the dispersion of paraffinic hydrocarbon was promoted by biochemical intermediates during fermentation. The Anthrone positive substances produced had a strong emulsifying activity. Zajic and Knettig (1972) also reported isolation of an interfacially active product from kerosine fermentation capable of emulsifying paraffinic hydrocarbons and No. 6 fuel oil (Table I).

The work herein is concerned with the degradation and emulsification of No. 6 fuel oil by three different bacteria of the pseudomonas type labeled J1, J3, and B2. Intermediates excreted during the biochemical oxidation of No. 6 fuel oil are capable of disrupting the large lump of water and oil (w/o) emulsion which is formed initially into small oil droplets. The resulting oil phase consists of oil pellets varying in sizes according to the bacterial activity.

Materials and Methods

Culture Conditions. The bacteria were isolated from municipal sewage by enrichment procedures. Cultures were purified however taxonomic. Identification of these isolates has not been completed at this time. The rod-shaped bacteria J1 and J3 synthesized yellow pigments when grown on liquid *n*-paraffin substrates. The curved rod-like B2 bacterium forms a white pigment and sometimes occurs in irregular clusters of cells. The aqueous mineral salts supporting medium has been described by Zajic and Supplisson (1972). One percent No. 6 fuel oil was added as a source of carbon. *N*-paraffins were sometimes tested at the levels specified. Pure culture experiments were conducted in 100 ml of sterilized culture broth (500-ml shake flasks) on a rotary shaker (200 rpm) at 23°C.

No. 6 Fuel Oil Recovery and Analysis. To help break the emulsion, the aqueous phase was acidified with H_3PO_4 to pH 2.0. The biomass was removed prior to oil extraction by centrifugation. The fuel oil remaining in the culture medium after degradation was extracted with chloroform and recovered by solvent evaporation in vacuum.

The changes of oil composition after bacterial degradation were determined by clay-gel adsorption chromatography. This technique was used to classify the fuel oil into the following hydrocarbon types: resins, aromatics, and saturates. Before clay-gel adsorption chromatography, the asphaltenes were removed by extraction with *n*-pentane using the method described in the American Society for Testing and Materials (1969).

The *n*-paraffins were extracted from the saturates fraction by adsorption in the vapor phase on 5A-type Molecular Sieve (Mortimer and Luka, 1967).

The paraffinic fraction was analyzed by gas–liquid chromatography. The apparatus used was a Hewlett-Packard model 5750 fitted with dual columns and a dual flame ionization detector. Columns were 3 ft × ⅛ in. o.d. of stainless steel and packed with 2.5% UC W98 on chromosorb G AW-DMCS (60–80 mesh). The sample size was 1 μl. of *n*-octane solution. The column temperature was programmed from 80°C (2-min hold) to 250°C at 10°C/min. The injection port temperature was 320°C and the detector temperature 285°C. Helium was used as the carrier gas at the flow rate of 80 ml/min. The F.I.D. was operated with the hydrogen flow rate of 55 ml/min and the air flow rate at 450 ml/min.

Extracellular Emulsifiers. Subsequent filtration (Whatman No. 2 oil removal), centrifugation (13,000 rpm), and repeated filtration (millipore 0.45 μ) steps were applied to obtain an oil- and cell-free supernatant.

Table I. Composition of No. 6 Fuel Oil, Wt %

Saturates	34.2
Aromatics	38.0
Resins	18.8
Asphaltenes	9.0
Sulfur	1.66
Gravity	0.968 SG 15°C

The extracellular emulsifier was precipitated from the supernatant by addition of three volumes of 95% ethanol at pH 2. The anthrone reaction was employed to establish the total carbohydrate content of the supernatant (Ashwell, 1957).

The degree of emulsifying activity has been estimated by determining under a microscope the size frequency distribution of oil globules in the emulsion stabilized in agar (Katinger et al., 1970).

Results

Fuel oil from culture broth was separated into asphaltenes, resins, aromatics, and saturates by clay-gel chromatography. The results are presented in Table II. Fol-

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Table II. Fractionation of No. 6 Fuel Oil by Clay-Gel Adsorption Chromatography

	No. 6 fuel oil composition, % w/w		Composition (% w/w) after bacterial biodegradation by		
Fraction	**Sample**	**Control**	**B2**	**J1**	**J3**
Saturates	34.8	34.9	27.0	29.0	27.0
Aromatics	38.8	36.7 (56.4)	39.3 (53.8)	38.9 (54.7)	36.9 (50.4)
Resins	18.1	18.1 (27.8)	21.6 (29.6)	20.1 (28.4)	22.6 (31.0)
Asphaltenes	8.3	10.3 (15.8)	12.1 (16.6)	12.0 (16.9)	13.5 (18.5)

The figures in parentheses indicate the percentage of that fraction to the total amount of aromatics, resins, and asphaltenes.
The control sample was No. 6 fuel oil agitated in fresh water and recovered the same way as biologically treated samples.

lowing chloroform extraction, an increase in asphaltene content can be seen in the control sample and in the samples degraded by bacteria. The proportions of aromatics and resins remained almost constant. The experiment showed a disappearance of waxes during biodegradation. In general, the reduction of saturate content was about 7% of the total oil weight.

The normal paraffin content was analyzed by gas liquid chromatography. Figures 1 and 2 show comparisons of chromatograms of the control saturate fraction and the saturate fraction recovered after 15 days of biodegradation carried out by bacteria B2, J1, and J3, respectively. A small amount of n-docosane was added to help locate the n-C_{22} peak (Figure 1B). Small peaks for iso-, or olefinic compounds can be observed within the range C_{19}–C_{24}. They became more noticeable in the biodegraded oil samples.

Figure 3 shows comparison of paraffinic hydrocarbons of No. 6 fuel oil extracted on molecular sieve and composition of this fraction after 15 days of biodegradation of bacterium B2. This No. 6 fuel oil possessed paraffinic hydrocarbons ranging from normal heptadecane (n-C_{17}) to nor-

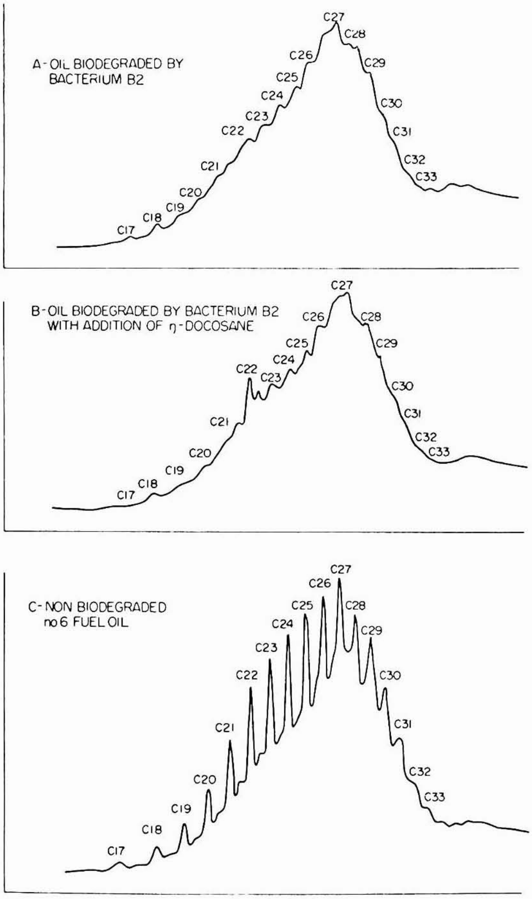

Figure 1. Removal of paraffinic hydrocarbons from No. 6 fuel oil by bacterium B2

A. No. 6 fuel oil after being biodegraded for 15 days by bacterium B2. *B*. Same as *A*, except *n*-docosane was added as a marker. *C*. Nonbiodegraded control

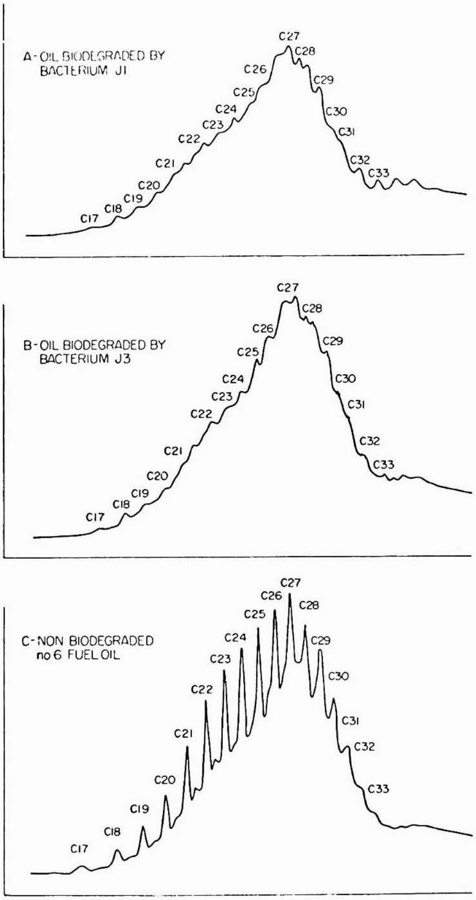

Figure 2. Biodegradation at No. 6 fuel oil by bacterial cultures J1 and J2

A. Removal of paraffinic hydrocarbons by culture J1. *B*. Removal of paraffinic hydrocarbons by culture J2. *C*. Nonbiodegraded No. 6 fuel oil (control) mal tritriacontane (n-C_{33}) without any discontinuity. All three bacteria (J1, J3, B2) reduced the normal paraffin content.

Emulsifying properties of microbial extracellular product(s) were studied. The research described was restricted to the cultivation of bacterium B2. The recovered cell-free supernatant produced partial disruption and breakup of a 1% freshly added oil phase into 1–10 mm long threads after 24 hr of rotary shaking. The aqueous phase stayed clear. The control sample produced only a big lump of w/o emulsion. The presence of a material within the cell-free supernatant capable of surface activity, which caused stabilization of oil globules in the water phase, could thus be postulated. This material can be precipitated from the aqueous solution by addition of ethanol.

Cultivation of bacterium B2 on the standard supporting medium was carried out with the No. 6 fuel oil substrate replaced by either n-dodecane, n-tridecane, n-pentadecane, n-heptadecane, or glucose as the sole source of carbon. The emulsifying activity of all the different types of supernatants recovered was determined on 1% (w/w) of No. 6 fuel oil. Results are summarized in Table III. The extracellular material in the supernatant from the B2 culture grown on n-dodecane exhibited the most effective emulsification activity. The test oil phase was broken up into pellets ranging from 0.1–1 mm in diameter while the aqueous phase had a mean oil globule size of 2 μ. A general appearance of the aqueous phase was brown. A similar effect resulted when n-pentadecane and glucose were used as a substrate. The culture supernatant from the glucose, however, produced only partial disruption of the oil phase into threads and globules (1–5 mm in diameter). A clear aqueous phase and only partial disruption of the oil phase (threads) was produced by a culture supernatant when hexadecane was used as a substrate.

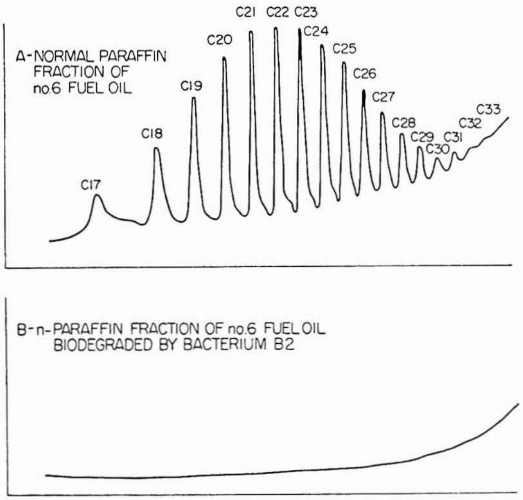

Figure 3. Biodegradation of No. 6 fuel oil: removal of paraffinic hydrocarbons from C_{17} to C_{33} by culture B2. Fuel oil was extracted on a molecular sieve to improve resolution of the peaks *A*. Control. *B*. Biodegraded sample

All the supernatants tested contained polysaccharides which gave a positive reaction to the anthrone test. In general, the anthrone assay results could only be correlated with the degree of surface activity except in systems where glucose was the sole source of carbon.

Because of the preferential growth of bacteria on normal paraffins, tests were conducted to determine whether improved emulsification could be obtained by addition of paraffins to No. 6 fuel oil prior to inoculation with bacteria. n-Dodecane was chosen as the substrate supplement. Culture B2 was cultivated on either No. 6 fuel oil or a mixture of n-dodecane and No. 6 fuel (1:1). The addition of n-dodecane to the basic No. 6 fuel oil substrate increased the oil emulsification rate and also gave a greater dispersion of oil in the aqueous phase. Results are summarized in Table IV. After 112 hr, the oil fraction in the aqueous phase consisted of 11% of the total oil when the combination paraffin–fuel oil substrate was used. This is compared to 5% of total oil dispersed in the aqueous phase when No. 6 fuel oil was used.

Oil spills which challenge the environment take place over a large temperature range. To evaluate the effect of temperature on the emulsification process, a series of experiments on various emulsion systems were conducted at temperatures of 6°, 12°, or 23°C. Table V shows the temperature effect upon the rate of oil dispersion. In all the culture systems the growth was reduced and dispersion was minimal at low temperatures. The necessary period of time to initiate oil dispersion was longer when the carbon substrate consisted of No. 6 fuel oil. The emulsification effect of the extracellular product tested by itself remains almost unaffected by a decrease of temperature.

Tests were carried out to evaluate the effect of in-

Table III. Fuel Oil Dispersion by Cell-Free Supernatant Produced by B2 Culture from Various Carbon Sources[a]

Cell-free supernatant[b]		No. 6 fuel oil dispersion			
Carbon source for B2 growth	Extracellular material concentration, ppm	Oil pellet mean diameter (oil phase)	Oil globules (aqueous phase)		Comments
			Size	Distribution	
n-C_{12}	210	0.1–1 mm	3 μ less 3 μ–8 μ 8 μ–15 μ	77% 15% 8%	Larger oil aggregates also occur in the oil phase
n-C_{15}	253	0.1–1 mm	3 μ less 3 μ–6 μ	79% 21%	Oil aggregates; pellet proportion less important than previously
n-C_{16}	218	None	Clear aqueous phase		Partial disruption of oil phase in threads
Glucose	272	1–5 mm	3 μ less 3 μ–6 μ	25% 75%	Same as above; oil spreading on the water surface

[a] The evaluation was conducted after four days of rotary shaking at 23°C ± 2. [b] From seven-day-old B2 bacterial culture. [c] Recovered by precipitation with 95% ethanol.

Table IV. Effect of n-C$_{12}$ Addition to No. 6 Fuel Oil During Bacterial Growth of B2

Temperature, 23 ± 2°C

Degree of dispersion by bacterial culture B2

	0.5% n-Dodecane + 0.5% No. 6 fuel oil			1% No. 6 fuel oil (control)		
		Aqueous phase oil globules			Aqueous phase oil globules	
Time of incubation hr	Oil phase appearance	Size	Distribution	Oil phase appearance	Size	Distribution
0	Black patch	Colorless		Black patch	Colorless	
42	Pellets, 0.1–1 mm	Colorless		Patch	Colorless	
65	Pellets, 1–5 mm	0.5–2 μ	77%	Pellets, 0.1–1 mm	Colorless	
		2–5 μ	18%			
		5–10 μ	4%			
		10–15 μ	1%			
90	Pellets, 1–5 mm		Brown	Pellets, 0.05–5 mm	Colorless	
112	Pellets		Brown	Pellets,		Brown
	1–5 mm	0.5–2 μ	76%	0.05–5 mm	2 μ	90%
					10 μ	
		2–5 μ	21%		20 μ	3%
		10–15 μ	1%		50 μ	5%
		11% of total oil			15% of total oil	

Any oil globule of size less than 50 μ is considered to be part of the aqueous phase.

Table V. Temperature Effects on Emulsification Process

Hydrocarbon, % w/w						Oil emulsification, oil globule diameter			
							Aqueous phase		
No. 6 fuel oil	n-C$_{12}$	Supporting medium	Inoculum	Temp, °C	Time for dispersion to begin, days	Oil phase, size mm	Oil size	Oil concn, ppm	Color
0.5	0.5	[a]	B2	23	2	0.1–1	2 μ	1100	Brown
0.5	0.5	[a]	B2	12	4	0.1–1	2 μ	165	Brown
1.0	—	[a]	B2	23	3	0.1–5	2 μ	505	Brown
1.0	—	[a]	B2	12	9	0.1–5	—	—	None
1.0	—	[b]	—	23	0.8	0.1–2	2 μ	43	Brown
1.0	—	[b]	—	6	1.2	0.1–2	2 μ	—	Brown
1.0	—	2 + 1% NaCl	—	23	0.8	1–2 + patch	2 μ	38	Brown
1.0	—	2 + 1.5% NaCl	—	6	1.2	1–2 + aggregates	5 μ	—	Brownish

[a] Mineral salts medium. [b] Cell-free supernatant from seven-day old B2 culture grown on n-C$_{12}$.

Table VI. Salt Tolerance of Emulsification Systems[a]

The evaluation was conducted at 23°C ± 2, 24 hr after addition of 1% w/w of fuel oil

No. 6 Fuel Oil Dispersion

		Aqueous phase				
		Oil globule				
NaCl, % w/w	Oil pellet mean diameter, mm	Size	Distribution, %	Color	Oil content, % w/w	Comments
0	0.1–2	2 μ less	94	Brown	0.4	
		2 μ–6 μ	5			
		6 μ–9 μ	1			
1.0	1–2	2 μ less	95	Brown	0.3	Most of oil stays as a patch on water surface
		2 μ–6 μ	4			
		6 μ–9 μ	1			
2.0	1–2	2 μ less	~99	Brown-green	0.3	Same
3.0	1–2	1 μ less	~99	Greenish		Same
3.5	1–2			Clear		Same

[a] The system consisted of cell-free supernatant of seven-day-old bacterial broth of B2 grown on normal C$_{12}$.

creased salinity upon the emulsification process. Addition of sodium chloride at different concentration levels was chosen to simulate seawater conditions. The test solution consisted of the cell-free supernatant from a seven-day-old culture of B2 grown on *n*-dodecane, NaCl, and 1% No. 6 fuel oil.

Table VI shows that oil dispersion became more difficult as the sodium chloride concentration increased. The dispersion test was conducted for 24 hr. At a 3% NaCl concentration, the agitated system produced a patch of surface oil and oil pellets from 1–2 mm in diameter. The aqueous phase had a greenish appearance and contained a nonmeasurable amount of oil.

Discussion

When No. 6 fuel oil is spilled in water undergoing agitation, w/o emulsions containing 50% water or more in the oil phase are formed within 24 hr. Greenlee (1960) showed that the water droplets induced the flucculation of asphaltene micelles present in the oil phase. They subsequently became encased in a film of precipitated asphaltenes.

When the system is inoculated with bacteria, the microorganisms which behave like hydrophilic colloids are easily trapped and bound in the water capsules within the emulsion. The stability of the large single lump of w/o emulsion was shown in our experiments to be affected after two or three days of bacterial action. The lump broke ultimately into pellets of 1–5 mm average diameter as shown in Figures 4 and 5.

During biodegradation, the bacteria metabolized the less refractile compounds—i.e., small molecular weight hydrocarbons in No. 6 fuel oil. The clay-gel chromatography analysis showed a reduction of the saturate fraction. The slight decrease in the percentage of aromatics and the relative increase of resins might be related to each other; however, this could not be readily ascertained. Part of the aromatics appeared to stay bound to the clay packing and thus could be recovered from the bed later with the benzene–acetone mixture as a part of the resin fraction. It is also possible that a portion of aromatics was attached to the asphaltene fraction. Yet the possible biodegradation of aromatics was not excluded to account for the slight weight reduction of this fraction.

The results show it is unlikely that asphaltenes and resins fractions undergo any microbial degradation which would lead to their partial removal. Studies conducted separately on purified asphaltenes show they are almost very resistent to biodegradation. The increase of the asphaltene content seemed to be associated with the solvent recovery procedure rather than with biodegradative action. This effect was attributed to polymerization promoted by chloroform.

Gas–liquid chromatography of the saturates fraction showed more specifically an expected selective removal of paraffinic hydrocarbons. The complete normal paraffin profile ranging from normal heptadecane to normal tritriacontane disappeared during bacterial degradation of the oil. After 15 days of microbial activity, no definite conclusion could be made showing a preferential degradation of any particular paraffinic hydrocarbon.

Other hydrocarbons such as nonlinear saturates and naphthenes may undergo oxidation or, in some cases, cooxidation. Consequently, the intermediate products may have very different structures.

The extracellular material recovered from microbial broth possessed emulsifying properties. Preliminary tests for carbonhydrates indicate the emulsifier has a polysaccharide structure.

Greater amounts of the extracellular product were recovered after growth of bacterium B2 on an aqueous substrate containing pure dodecane. Better emulsification of the oil phase was also observed using the product derived from this substrate.

The temperature and salinity affected only slightly the activity of extracellular emulsifier.

It can be concluded that microbes may play an active role in the biodegradation and dispersion of No. 6 fuel oil when it is spilled in fresh or marine water. The bacteria reported herein metabolize the paraffinic hydrocarbons present in the oil and convert the paraffinic hydrocarbons into emulsifying materials. The extracellular emulsifying agent could be produced separately and added in pure form to obtain emulsification of No. 6 fuel oil under adverse environmental conditions.

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Received for review June 25, 1973. Accepted February 25, 1974.

Monitoring Narragansett Bay Oil Spills by Infrared Spectroscopy

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■ A 1973 oil spill on Narragansett Bay was monitored for 30 days using infrared spectroscopy. All samples of the spill collected during this period were traced to the source of the spill by computer matching of their infrared spectra. Two subsequent oil slicks found in the same general area were shown to be from a different source by the same method of analysis.

During the evening of April 9, 1973, an oil tanker struck an underwater object in Narragansett Bay approximately 10 miles from its destination in East Providence, R.I. The tanker was extensively damaged and ~100,000 gal. of No. 6 grade fuel oil were released into the Bay. On April 11, less than 48 hr after the spill, we started sampling the oil from the beaches and shallow waters near the shore. In this report we show that the source of the oil can be identified by infrared spectroscopy after more than 30 days of weathering on the open sea.

The infrared bands used to identify the oil and the computer analysis of the spectra have been discussed previously (*1*). Complete infrared spectra from 4000–400 cm^{-1} are recorded; however, 21 selected bands between 1200 and 650 cm^{-1} are used for the identification. For each of the known samples the peak heights of the 21 bands are converted into absorptivities, and these are stored in a computer file (if a band is not observed it is given a zero absorptivity and is eliminated from the analysis). To match an unknown with the correct known, the following procedure is carried out: The absorptivities of the bands in the spectrum of the unknown are calculated, the ratios of the absorptivities for an unknown to those of each known are calculated, these ratios are averaged for each known stored in the computer file, the percent difference between this average and each ratio is determined, and finally the number of bands with a percent difference less than a certain value (e.g., 5, 10, 25%) are listed. The unknown is matched to a known when most of its bands are within 5 or 10%.

Other methods to identify the source of oil spills by infrared spectroscopy have been suggested (*2-9*). The present analysis differs from the others in the type and number of bands used, and in the method of computer analysis. By use of our method, an unknown can be matched to the correct known (assuming that the required data for the known are stored in the computer file) in approximately 30 min; this includes the time required to measure the spectrum and perform computer analysis of the data.

Experimental

Infrared spectra of the samples taken from the tanker, the beaches, and the water were measured on a Perkin-Elmer Model 521 infrared spectrometer. The spectral slit width of the instrument was <2 cm^{-1} from 600–2000 and <4 cm^{-1} from 2000–4000 cm^{-1}. Samples taken from the beaches and water were collected in bottles and on aluminum foil. The techniques of using Al foil to collect samples and using the same foil as a sample "cell" for obtaining infrared spectra are discussed elsewhere (*10*). Oils adhere to the Al foil whereas water is repelled; thus, it is a very useful technique for obtaining spectra of oil-water emulsions. Most of the spectra were measured using AgCl windows in a 0.1-mm demountable cell; however, spectra of samples saturated with water were measured using the Al foil technique.

Table I. Samples Taken from Narragansett Bay Oil Spill

Known no.	Number of bands with % difference <10% with dates									
	4/11	4/12	4/15	4/16	4/17	4/19	4/21	4/22	5/1	5/10
101	6	5	6	6	6	7	3	3	3	5
102	2	1	1	2	2	2	1	2	0	1
103	1	2	1	2	2	3	1	3	2	1
104	1	2	1	1	1	2	2	2	0	1
105	3	2	1	2	3	3	2	3	1	3
106	3	3	3	3	2	3	3	1	1	2
107	6	6	6	6	6	6	4	3	3	5
108	3	2	2	3	3	3	5	3	1	1
109	4	3	4	4	3	3	0	3	1	4
110	0	1	0	1	0	1	1	2	0	0
111	2	1	1	2	2	2	1	1	2	1
112	3	2	2	2	2	2	1	3	0	2
113	5	5	5	5	5	3	2	4	3	4
114	3	3	3	3	3	3	2	2	1	1
115	1	1	0	2	1	2	1	2	0	0
116	4	6	7	5	4	5	3	5	2	5
117	5	5	5	5	5	4	3	2	2	4
118	3	3	3	3	3	3	3	2	1	2
119	2	2	2	2	2	3	1	2	1	1
120	2	2	2	1	0	1	2	1	2	1
121	0	0	0	1	0	2	1	0	1	1
122	3	0	3	3	2	3	2	0	1	2
123	2	3	2	2	3	1	2	3	1	0
124	5	6	3	4	3	4	5	5	4	2
125	3	4	3	0	1	1	2	2	1	2
126	2	1	2	3	2	3	2	1	0	0
127	2	2	2	2	2	2	2	1	2	1
128	4	3	4	2	2	3	4	3	2	2
129	6	4	5	4	5	6	4	4	3	5
130	3	4	3	3	3	3	2	3	3	2
131	2	2	2	1	2	1	1	3	1	1
132	3	2	2	2	2	3	2	3	2	1
133	3	4	3	4	4	3	3	2	2	3
134	1	1	0	1	0	1	0	1	2	0
135	2	3	2	2	2	3	3	2	0	1
136	2	1	1	2	2	2	2	0	1	2
137	1	1	1	1	1	1	2	1	0	1
138	10	9	10	10[a]	10[a]	8	9	7	7	9
No. of bands compared	10	9	10	10	10	10	10	7	8	9

[a] All bands within 5%.

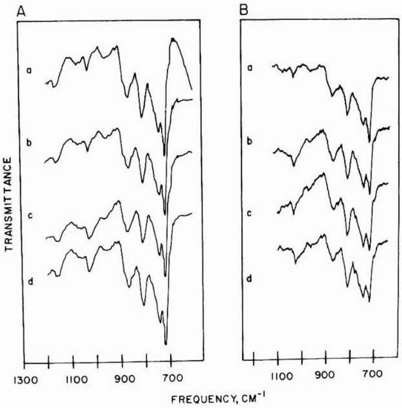

Figure 1. Infrared spectra (650–1200 cm^{-1}) of samples from the tanker, from Narragansett Bay and from another suspect source

(A) Comparison of spectra of samples from the tanker and from the vicinity of the spill (slick I): a, from the tanker; b, Bay sample taken on April 16, 1973; c, Bay sample taken on April 21; d, Bay sample taken May 10, (B) Comparison of spectra of two subsequent oil slicks with that of the tanker and a suspect source: a, from the tanker; b, slick II: c, slick III; d, oil from the suspect source weathered for 14 days on the roof of our laboratory. Spectra in A were measured using the conventional transmission method, whereas spectra in B were measured using the Al foil technique

Results and Discussion

To monitor the spill on Narragansett Bay we obtained a large sample of oil from the tanker involved in the accident. The infrared spectrum of this sample was recorded and the required data were stored along with 37 other knowns in the computer file. Spectra in the 650–1200 cm^{-1} region of a sample from the tanker and three samples taken from Narragansett Bay during the month following the accident are shown in Figure 1A. As can be seen, the only major spectral changes after 31 days of weathering are the shapes of the bands at 1020 and 1070 cm^{-1}. Even the weak bands and shoulders below 900 cm^{-1} remain constant with weathering.

The computer analysis of 10 samples taken from the Bay between April 11 and May 10 are listed in Table I. Each of the field samples is compared with 38 known samples of crude oils and their distillate products. The number of bands with a percent difference <10% are listed. The known sample taken from the tanker is #138. Comparison of the field samples with this known is almost perfect in all cases. Even after 31 days of weathering, 9 out of 9 bands compare within 10%. It should be noted that the field samples also compared favorably with nos. 101, 107, and 129; however, the comparison with no. 138 is always better.

Since the time of the original spill there have been two other minor oil slicks reported on Narragansett Bay. The first of these slicks (II) was found in early May about 12 miles south of the original shore deposits. It was reported in the local press that this slick also came from the original spill—i.e., the tanker. We obtained several samples of this new slick. Its spectrum (b) is compared with a sample from the tanker (a) in Figure 1B. Careful comparison of the spectra indicates that sample b is from a different origin. The major visual difference is the ratio of the two strong bands between 700 and 800 cm^{-1}. Computer analysis further confirmed our visual observations—i.e., absorptivities of the bands in the spectrum of this new slick were considerably different from those of known no. 138.

A third oil slick (III) was discovered on the Bay on June 4; a spectrum of this spill (c, Figure 1B) indicated a close similarity to the second slick (II). We felt that the two came from the same location, and we obtained a sample from the suspect source. After weathering the sample from the suspect source on the roof of our laboratory for 14 days its spectrum (d, Figure 1B) was very similar to those from slicks II and III. Our conclusion is that both slicks originated from the same suspect source.

In summary, we have shown that infrared spectroscopy provides a simple, rapid means of tracing the source of oil spills; coupled with computer analysis the identification can be performed in <30 min. At present, we have measured the infrared spectra of ~125 known samples of crude oils and their distillate products, and all have characteristic spectra which can provide positive identification. Furthermore, we have sampled five oil slicks on the open sea, and all of the results strongly support this method of analysis.

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Received for review November 16, 1973. Accepted March 18, 1974.

Cryogenic Separation of Methane from Other Hydrocarbons in Air

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■ Methane has a higher vapor pressure than any other hydrocarbon. Because of this, methane can be separated from the other hydrocarbons in ambient air by condensing the heavier ones on a suitably cold surface. A methane separator based on this idea has been constructed and tested with bottled gas mixtures. At the present stage of development, the device traps more than 95% of all the nonmethane hydrocarbons used and has no measurable effect on methane. When used with a total hydrocarbon analyzer, the separator establishes a baseline for nonmethane hydrocarbons, obviating the problem of setting an accurate hydrocarbon zero level.

Many of the hydrocarbon contaminants in air take part in the photochemical reactions that form smog, but methane, which occurs naturally at relatively high levels, does not. Studies (Environmental Protection Agency, 1970) have shown that methane typically is present at levels above 940 $\mu g/m^3$ (1.4 ppm) and constitutes perhaps half of the total hydrocarbon level in an urban atmosphere. The ratio of methane to nonmethane hydrocarbons varies so widely, however, that total hydrocarbon measurements do not accurately reflect smog generation potential. For this reason the Environmental Protection Agency (EPA) has set a national primary and secondary ambient air standard for hydrocarbons (*Federal Register*, 1971) specifying that the 6–9 a.m. 3-hr average of nonmethane hydrocarbons shall not exceed 160 $\mu g/m^3$ (0.24 ppm) more than once per year.

Methane in ambient air can be measured by gas chromatography using flame ionization detectors (Stevens et al., 1970). Systems that will automatically sample ambient air once each 5–15 min, measuring separately methane and total hydrocarbons, are commercially available and this method has been approved by the EPA (*Federal Register*, 1971). There are, however, reasons for considering other possible methods of measurement. Gas chromatography is inherently a batch process, requiring a few minutes per analysis, thus it cannot follow the more rapid hydrocarbon fluctuations that occur in urban atmospheres. Also, since this system and the requirement to correct for methane is fairly new, many air pollution agencies have total hydrocarbon analyzers but no method of discriminating between methane and other hydrocarbons. For them a relatively inexpensive modification to their sampling system would be preferable to purchase of a complete new instrument.

This paper describes a device based on a cryogenic trap that provides a useful separation of methane from other hydrocarbons. Results of tests performed in our laboratory are included. Evaluation of performance of this instrument for a wide range of ambient air conditions will be part of a comprehensive field test program planned for the next year.

Device Description

Examination of vapor pressure data for hydrocarbons (some extrapolated from higher temperatures) indicated that at temperatures near 77°K it should be possible to trap most hydrocarbon compounds to such an extent that their concentrations would be reduced to negligibly small levels in an air sample. At the same time, methane, at typical ambient air concentrations of a few parts per million, should pass through the trap. Thus a separation appeared possible using a cryogenic trap at liquid nitrogen temperature.

The basic methane separation device is a cooled tube (trap) through which air flows before entering a total hydrocarbon analyzer (THC). At the optimum temperature, methane concentration in the air is unchanged, while concentrations of the heavier hydrocarbons and many other air contaminants are reduced, most to negligibly small amounts. The THC then measures the methane level with very little interference from other compounds. A temperature around 80°K will cause good separation between methane and other hydrocarbons. Liquid nitrogen boils at 77°K, is readily available and not expensive, so it was used as the coolant in our work to date.

To operate this device with ambient air for reasonable lengths of time, several additions to the basic trap were made. The flow diagram of the current version of a methane separator is shown in Figure 1. Timer-controlled valves have been added alternately to supply ambient air or processed air to the THC. Thus the THC alternately measures total hydrocarbons or methane. Levels of hydrocarbons, methane corrected, are obtained by subtraction.

Oxygen will condense from ambient air at 77°K and will eventually fill the trap with liquid. This can be avoided by operating the trap at a partial vacuum (less than about 24 in. of mercury absolute). The pump on the outlet and

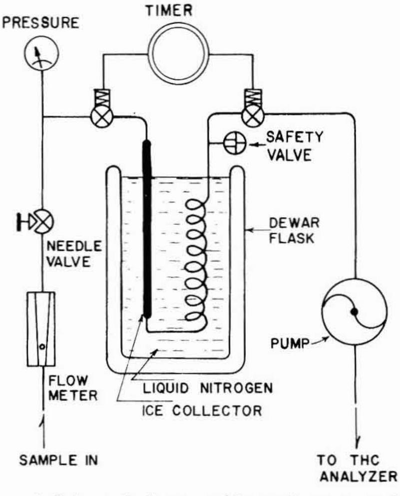

Figure 1. Schematic diagram of the methane separator

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Table I. Percent of Various Hydrocarbons That Pass Through Trap

Component	Dew Point of Input Gas Stream, °C		
	−60	1	25
CH_4	100	100	100
C_2H_4	33	<2[a]	2.5
C_2H_6	17	<2	<2
C_3H_8	28	<2	<2
i-C_4H_{10}	33	<2	<2
n-C_4H_{10}	33	<2	<2

[a] < indicates the concentration was below the level indicated. The value shown is the minimum level for reliable detection.

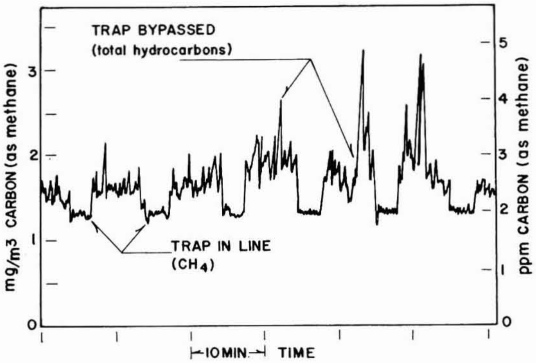

Figure 2. Typical data from a total hydrocarbon monitor when used with the methane separator. This recording was obtained at about 2:00 p.m. in downtown Eugene, Ore.

needle valve on the inlet combine to keep the pressure in the trap low enough to avoid oxygen condensation and also provide the sample at the pressure required by the Beckman Model 400 THC used.

Water also condenses and the larger diameter inlet section avoids clogging the trap with the relatively large amounts of ice formed. The present trap in the methane separator consists of a 6 in. long ½-in. diameter stainless steel entrance section followed by a 160-in. length of ¼-in. o.d. copper refrigeration tubing.

Development and Testing

During development, several lengths and diameters of stainless steel, copper, and Teflon were tried. The material seems to have little effect on separator performance. Tubing diameter must be large enough to avoid clogging with ice or CO_2 but for a given sample flow rate it has little effect on performance otherwise. Flow rate and trap length are the primary variables that have significant effect on the efficiency with which the trap collects heavier hydrocarbons. In general, the lower the flow rate or the longer the trap, the better will be the trap efficiency. The specific relationship remains to be worked out.

Laboratory Tests

The ability of this device to separate methane from other hydrocarbons was checked in our laboratory using bottled gas mixtures. One mixture contained about 10 parts per million (ppm) each of methane, ethane, propane, isobutane, and normal butane in air, the other mixture about 2 ppm each of methane, ethylene, and propane in nitrogen. The air mixture contained about 5–10 ppm water vapor (dew point −65° to −60°C). Dew point of the nitrogen mixture was not available, but it was also apparently very dry compared to ambient air.

Separator performance was measured using a Hewlett-Packard 7620 series gas chromatograph and flame ionization detector. The column was 6 ft Porapak Q in ⅛ in. stainless steel. Carrier was N_2 at 40 cc/min, and the oven was programmed from 70–150°C. System sensitivity was such that hydrocarbon concentrations between 1% and 2% of the levels in the test gases could be reliably detected. Hydrocarbon peak heights were measured for samples of gas leaving the separator and these values were compared with peak heights from samples of the inlet gas to determine change in concentrations of the various hydrocarbons.

In one series of tests, only bottled gas was admitted to the separator after the trap was cooled. Initial separation was good. Methane was unchanged and no other hydrocarbons were detected in the trap effluent. In a short time, however, the other hydrocarbons began to break through, and the various output hydrocarbon levels stabilized in 15–60 min at the amounts shown in the left-hand column of Table I.

Better separation efficiency was observed after normal room air had been admitted to the trap. This prompted addition of water vapor to the test gas stream, done by bubbling finely dispersed test gas through water, resulting in a dew point near the water temperature. Tests were performed using water temperatures of 1° and 25°C. Results are shown in the center and right-hand columns of Table I.

With water vapor in the inlet gas, behavior was more stable and separation efficiency much improved. Concentrations of many of the heavier hydrocarbons were below the minimum level for reliable detection (1–2% of input). From this data it appears that more than 95% of the nomethane hydrocarbons were collected while methane was not significantly effected.

When moist test gas mixtures were used, only ethylene showed any measureable variation in output concentration. Early in a test at a dew point of 1°C, ethylene output concentration was as high as 12% of the input. This decreased steadily to below detectable limits (1.6%) in 2 hr. In another test with the gas stream at a dew point of 25°C, the ethylene peak was initially 2.5% of input, and it remained at or below this level throughout the test.

This device was also operated at the Lane Regional Air Pollution Authority's continuous air monitoring station in Eugene, Ore. The separator was connected into the sample line just before the sample reached their Beckman Model 400 THC. The separator operated on a 10-min cycle, alternating between a 3-min period with the trap in line and a 7-min one with the trap bypassed. A typical strip chart recording of the THC output is shown in Figure 2. The relatively stable lower level sections of the trace were obtained when the sample passed through the trap before reaching the THC, and should represent primarily CH_4. The higher, more variable parts of the record resulted when the sample bypassed the trap and indicate total hydrocarbon content of the ambient air. Operated in this manner, the device establishes a new baseline corresponding to the relatively stable CH_4 levels, above which nonmethane hydrocarbon levels are measured.

Discussion

In these laboratory tests this system does appear to provide a useful separation of methane from other light hydrocarbons. In the tests performed using moist air or nitrogen as the diluent, well over 95% of the nonmethane hydrocarbons were trapped, while methane level was not measureably changed. The presence of relatively large amounts of water vapor compared to the amount of hydrocarbons is necessary for this performance. In very dry conditions it may be useful to add water vapor to the gas stream as was done in our tests with bottled gas.

Use of this separator with a total hydrocarbon monitor makes it possible to monitor ambient total hydrocarbon levels most of the time with the speed of response of the total hydrocarbon monitor, and to sample the relatively stable methane levels periodically. This method essentially generates a new baseline, corresponding to the CH_4 level, above which nonmethane levels are measured. Sinnce the standards do not require measurement of the actual level of methane, it is only necessary to set the span of the THC accurately. The exact zero setting no longer effects the data, so the troublesome problems of setting an accurate zero are eliminated.

Acknowledgment

To aid in this work the Lane Regional Air Pollution Authority provided a grant of equipment and the use of their Continuous Monitoring Station in downtown Eugene. Discussions with Ron Nance of LRAPA and R. K. Stevens of EPA have been most helpful.

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Received for review September 10, 1973. Accepted January 18, 1974. This work was supported by the National Science Foundation, RANN grant 33017x, and by the Lane Regional Air Pollution Authority.

Algal Blooms—Possible Effects of Iron

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■ Iron, in concentrations of 0.1–1.0 mg/l., causes a shift in the dominant type of algae grown in batch cultures from relatively unobjectionable greens to the scum-forming blue-greens, without causing a significant change in the total algal biomass. Results were not dependent on the manganese concentration (0–0.40 mg/l.) or the phosphorus concentration (0.07–7.0 mg/l.).

Perhaps the most widely publicized method of controlling excessive algal growth in a lake is by limiting an essential nutrient, such as the removal of phosphorus from sewage effluents and detergents. However, not all types of algae are equally troublesome in eutrophication problems. Blue-green algae, which form surface scums and cause odors, are very undesirable at typical algal bloom concentrations of 6–12 mg/l. (dry weight) while the same amounts of green algae are not so objectionable. It is therefore important to understand the chemical and physical conditions that control the dominant algal type.

It is well known that certain factors, both natural and man caused, can increase the green to blue-green algal ratio (G/BG), without necessarily changing the total algal biomass. The diversion of domestic sewage effluent away from a lake can cause the G/BG to increase as does aeration, mixing, and upwelling. Symons (1969) and coworkers, Bernhardt (1967), Wirth et al. (1970), and others have documented the increase in the G/BG and the changes in water chemistry when small lakes and reservoirs are mixed mechanically or with compressed air. Shapiro (1973) and King (1970) feel that low CO_2 concentrations and high pH favor blue-greens and that the increase in the G/BG with aeration is due to increased CO_2. Our previous work (Morton et al. 1972) on CO_2 and eutrophication showed that both greens and blue-greens can efficiently utilize CO_2 at very low concentrations and high pH, but we worked with individual algae species and not mixtures. Bella (1970) feels that aeration and mixing favor the denser species. Guseva (1952) and Patrick et al. (1969) have studied the effects of manganese and concluded that high manganese concentrations inhibit the blue-greens more than the greens and diatoms. Gerloff and Skoog (1957), using the blue-green alga *Microcystis,* found that iron antagonizes or reduces the manganese toxicity.

Procedure

We have studied in the laboratory the effects of iron and manganese on the G/BG in mixtures of algae grown in batch cultures. Algae used were the green algae *Chlorella pyrenoidosa* (Wis 2005), *Dictyosphaerium pullchellum,* and *Selenastrum capricornutum;* and the problem-causing blue-green algae *Anabaena circinalis* (Wis 1038), *Gloeotrichia echinulata* (Wis 1052), and *Microcystis aeruginosa* (Wis 1036). The growth medium was Hughes' (1958), modified to contain 15 mg/l. N as $NaNO_3$, 0.07–7.0 mg/l. P as K_2HPO_4, 10 mg/l. Ca as $CaCl_2$, 7 mg/l. Mg as $MgSO_4$, 20 mg/l. Na_2CO_3, 6 mg/l. citric acid, and 25 mg/l. Na_2SiO_3. EDTA was not present except where noted. The medium was prepared using double glass distilled water. The light intensity was 150 ft-candles and the temperature was 23-25°C. The growth of each type of algae was followed by cell counts, while the total algal growth was also monitored by spectrophotometric measurements at 600 $m\mu$. Manganese was added as $MnCl_2 \cdot 4H_2O$ in the concentration range of 0-1 mg/l. Iron was added as $FeCl_3 \cdot 6H_2O$ in the concentration range of 0.01-2 mg/l. Data were taken at various growth times with total algal growth from 8-150 mg/l. The initial pH range of the various solutions was between 7.2 and 7.8, which is satisfactory for both greens and blue-greens. The controls showed iron was not toxic to any of the individual algal species but that manganese did exhibit increasing

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Table I. Growth of Chlorella–Anabaena Mixtures as Function of Iron, Manganese, and Phosphorus

Iron, mg/l.	Total algae, mg/l.	G/BG[a]	Total algae, mg/l.	G/BG[a]
	P = 7.0 mg/l.			
	Mn = 0.00 mg/l.		Mn = 0.10 mg/l.	
0.10	10	>100	13	>100
0.30	9	>100	13	>100
1.0	12	3.1	19	0.51
2.0	15	0.32	36	0.13
	P = 1.4 mg/l.			
	Mn = 0.30 mg/l.		Mn = 0.60 mg/l.	
0.10	27	>100	21	>100
0.30	24	1.9	22	3.2
0.60	24	3.9	25	0.78
2.0	24	1.9	27	0.78
	P = 0.21 mg/l.			
	Mn = 0.10 mg/l.		Mn = 0.40 mg/l.	
0.05	9	35	18	16
0.20	12	0.26	12	0.86
1.0	12	0.32	15	0.44
	P = 0.07 mg/l.			
	Mn = 0.00 mg/l.		Mn = 0.40 mg/l.	
0.05	11	>100	17	14
0.20	11	5.0	25	0.91
1.0	12	0.33	23	0.24

[a] Green to blue-green algal ratio as determined by cell counts.

Table II. Growth of Chlorella–Gloeotrichia Mixtures as Function of Iron, Manganese, and Phosphorus

Iron, mg/l.	Total algae, mg/l.	G/BG[a]	Total algae, mg/l.	G/BG[a]
	P = 1.4 mg/l.			
	Mn = 0.00 mg/l.		Mn = 0.10 mg/l.	
0.01	60	>100	—	—
0.05	—	—	60	21
0.10	66	4.8	72	13
0.30	60	0.07	57	2.2
1.0	72	0.01	96	0.05
	Mn = 0.30 mg/l.		Mn = 0.60 mg/l.	
0.10	90	24	42	5.0
0.30	72	6.5	66	4.4
0.60	54	0.38	42	3.2
	P = 0.07 mg/l.			
	Mn = 0.00 mg/l.		Mn = 0.10 mg/l.	
0.05	9	>100	11	>100
0.20	12	17	11	4.9
1.0	13	2.3	18	0.61

[a] Green to blue-green algal ratio as determined by cell counts.

toxicity with concentration to the blue-greens but not to the greens.

Results and Discussion

A few typical results are shown in Tables I and II for *Anabaena–Chlorella* and *Gloeotrichia–Chlorella* mixtures. In general, as the iron concentration increased the growth of the blue-greens was stimulated more than the greens. At about 0.1–1.0 mg/l. of total iron the blue-greens started to dominate over the greens. At manganese concentrations of over 0.4 mg/l., we usually did not see a complete blue-green dominance at high iron as we did at lower manganese levels, but nevertheless there was usually a general decrease in the G/BG with increasing iron. We attribute this to the blue-green toxicity of manganese at these high levels. We found no universal relationship between the G/BG and the iron to manganese ratio, since the stimulation of blue-greens by iron occurred even with no manganese present. The G/BG's showed similar trends over a total algal biomass range of 8–150 mg/l. in any given experiment, though they did vary somewhat in absolute magnitude.

The green algae *Selenastrum,* the selected species for standardized tests evaluating the nutrient potential of natural waters (EPA, 1971), and *Dictyosphaerium,* a filter clogging alga which causes problems in the Great Lakes, were substituted for *Chlorella* in experiments using *Anabaena* and *Microcystis,* and results similar to those in Tables I and II were obtained.

We do not know what is the mechanism of the stimulation of the blue-greens by iron; however, we can rule out a few possibilities. We obtained similar results over a phosphorus concentration range of 0.07–7.0 mg/l. Therefore, it seems unlikely that the iron is tying up the phosphorus, thereby permitting the blue-greens to dominate due to more favorable phosphorus uptake kinetics. We also obtained similar results with no EDTA as we did for EDTA concentrations of 0.01, 0.10, and 1.0 mg/l. This minimizes the possibility that iron may be coagulating some impurity that is toxic to the blue-greens but not to the greens, since EDTA is often used to complex metals that are toxic to blue-green algae.

Microcystis was used as a representative of objectionable blue-green algae that are not capable of fixing nitrogen; the results were the same as with the blue-green algae *Anabaena* and *Gloeotrichia* that are nitrogen fixers. Therefore, the effects of iron are probably not related to nitrogen metabolism.

In conclusion, increases in the total iron, even when already present in excess, favor some common species of blue-greens over some greens. Therefore, consideration should be given to the total dissolved and colloidal iron in effluents. One example of this is in some wastewater phosphorus removal processes that use excess $FeCl_3$ to precipitate the phosphorus. We also feel there are undoubtedly many factors that can affect the G/BG in a lake and that this report should be taken only to emphasize iron as one of them rather than to deemphasize the others.

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Received for review November 12, 1973. Accepted March 7, 1974. Work supported by EPA Grant R801168.

Valence Formulas for $C_2H_3NO_5$—PAN or APN?

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■ Simple valence considerations suggest that the compound with the formula $C_2H_3NO_5$ is better formulated as peroxyacetylnitrate (PAN) rather than as acetylpernitrate (APN).

It is now well accepted that one of the more objectionable compounds formed in the atmosphere by reactions between automobile exhaust gases and oxygen or ozone, has a molecular formula $C_2H_3NO_5$ (Stephens, 1969). Until recently, the structure of this compound has been given as $CH_3(CO)OONO_2$ peroxyacetylnitrate or PAN (Stephens, 1969) formed according to Reaction 1. However, Hanst (1971) has presented evidence that NO_3 and acetyl, rather than NO_2 and peracetyl, are the species which give rise to $C_2H_3NO_5$. Although he favors the Reaction 2 giving acetylpernitrate (APN), Hanst concedes that the reaction could also produce PAN.

$$CH_3(CO)OO + NO_2 \longrightarrow CH_3(CO)OONO_2 \quad \text{PAN} \qquad (1)$$

$$CH_3(CO)O + NO_3 \longrightarrow CH_3(CO)ONO_3 \quad \text{APN} \qquad (2)$$

The acetylpernitrate (APN) has been formulated "without an oxygen-oxygen bond" (presumably between a carbon and a nitrogen atom), and the observation of oxygen evolution and nitrite ion formation on hydrolysis has been rationalized in terms of the pernitrate ion, NO_4^- (Hanst, 1971). However, there is little information available on the structure of this ion (Moeller, 1952) and pernitric acid may be formulated either as $NO_2.O.O.NO_2$ plus n-H_2O (Mellor, 1928) or $HOONO_2$ (Schwarz, 1948).

In this communication, we shall demonstrate how simple bonding theory for $RONO_3$ ($R{=}CH_3CO$) suggests that the molecule is better formulated as PAN rather than as APN. To do this, we shall make the following assumption. Because the Pauling electronegativities (Pauling, 1960) of nitrogen and oxygen atoms (3.0 and 3.5) are not very different, stable valence formulas should have small formal charges on these atoms when they are adjacent in neutral molecules. For illustrative purposes, we shall endeavor to make these charges zero, sometimes using new techniques (Harcourt, 1971, 1972 a,b).

For $RONO_3$, it is possible to construct Lewis-Pauling valence-bond formulas thereby obtaining four structural isomers for this molecule, (1)-(4) of Chart I. By means of the mechanisms shown in Chart I, decomposition of isomers (1)-(3) into singlet O_2 and acetyl nitrite (RONO) reduces the nitrogen and oxygen formal charges to zero, thereby rendering these isomers unstable.

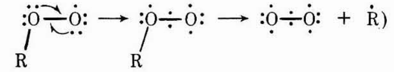
(The valence formula:

$$:\ddot{O}=\ddot{O}:$$

with all electrons spin paired, represents a singlet-spin excited state for oxygen. It can be generated from Lewis acid-base reactions, a few examples of which are the decompositions above. The triplet-spin ground state of oxygen has two unpaired electrons with parallel spins, and (omitting spin designations here) the valence formula for it,

$$:\dot{\underset{\cdot}{O}}\div\dot{\underset{\cdot}{O}}:$$

may be generated from the molecular orbital configuration (Green and Linnett, 1960; Linnett, 1972). It has been deduced (Harcourt, 1972a) that triplet oxygen may be formed as follows, by the free radical decomposition $RO_2\cdot \rightarrow R\cdot + O_2$:



Isomers (4), (5), and (6) with the NO π-bond for the nitro group of (6) resonating between two positions, should be more stable. Structure (5) was not considered by Hanst. Lachowicz and Kreuz (1967) examined a similar structure $R_1R_2CHOONO$ ("superoxynitrite") for the product of the low-temperature reaction between dinitrogen tetroxide, oxygen, and olefins. However, these workers showed with both chemical and spectroscopic data, that the product had the structure $R_1R_2CHOONO_2$—i.e., similar to PAN (6). It might be argued that the formal charges of (6) can also generate decomposition according to the mechanism in Chart II, but this does not reduce the magnitudes of the formal charges. Further, (6) and (7) should participate appreciably in resonance, but of course the ON bond will be weakened.

Chart I

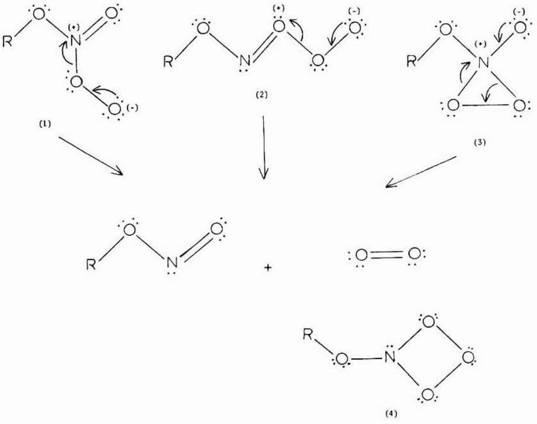


Chart II

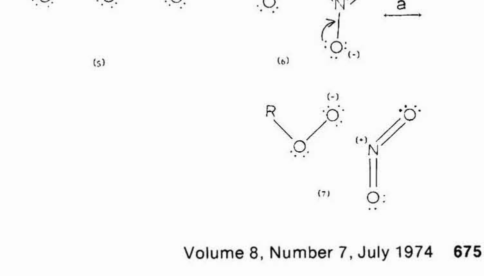


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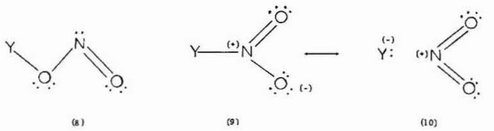
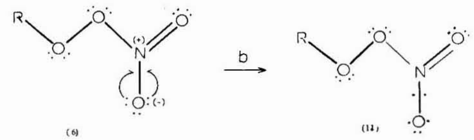
Chart III



The resonance of (6) $\overset{a}{\leftrightarrow}$ (7) is expected to help stabilize the PAN isomer relative to isomers (4) and (5). For N_2O_3, two isomers are known (Varetti and Pimentel, 1971), namely sym ONONO and asym $ONNO_2$; their valence-bond formulas, namely (8) and (9) $\leftrightarrow$ (10) with Y = N=O in Chart III, are similar to (5) and (6) $\overset{a}{\leftrightarrow}$ (7). The asym isomer has been estimated (Varetti and Pimentel, 1971) to be more stable by about 5 kcal/mol. When Y = F in (8)-(10), the nitrosyl and nitryl isomers ONOF and FNO_2 are obtained. ONOF has been synthesized recently, and can be isomerized (Bruna et al., 1971) to FNO_2. However, when Y = CH_3 in (8)-(10) (methyl nitrite and nitromethane), the contribution from (10) to the resonance stabilization of (9) will be small because of low electronegativity of the methyl group.

Chart IV

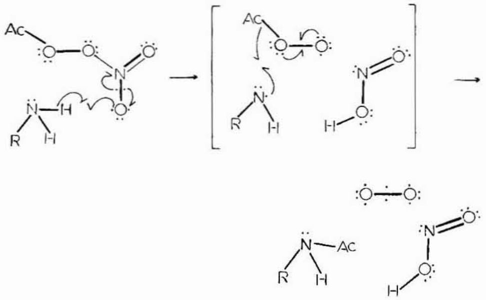


On reaction with OH^-, $C_2H_3NO_5$ liberates CH_3COOH + NO_2^- + singlet O_2 (Mudd, 1966; Stephens, 1967; Steer et al., 1969). The action of OH^- on isomers (4), (5), and (6) generates three NO_4^- isomers each of which can decompose into NO_2^- + singlet O_2.

It is possible to reduce the magnitudes of the formal charges in the valence-bond formulas (6), (7), (9), and (10). Recently, one of us has shown that this may be done for nitro groups by delocalizing oxygen nonbonding electrons into vacant bonding NO orbitals (Harcourt, 1971, 1972a). The quantum mechanical details for this type of delocalization have been described on numerous occasions elsewhere (Harcourt, 1971, 1972a,b), and we need only note the result here. Thus, (6) $\xrightarrow{b}$ (11) (Chart IV) thereby stabilizing (11) relative to (6) by increasing the number of electrons which participate in bonding and reducing simultaneously the magnitude of the formal charges to zero. Valence formula (11) with two extra bonding electrons is an example of an "increased-valence" formula and it can be shown to be more stable than (6) (Harcourt, 1971, 1972a,b). From (7) and (10), "increased-valence" formulas may also be generated with extra stability and smaller formal charges. However, these "increased-valence" formulas would have nonzero formal charges and therefore will be less important than those obtained from (6) and (8). Some specific examples are discussed elsewhere (Harcourt, 1971).

Recently, Wendschuh et al. (1973) have studied the reactions of $C_2H_3NO_5$ with some primary amines. The products for each of these reactions were an acetamide, nitrous acid, and molecular oxygen. If one uses the "increased-valence" structure (11) for PAN, and the $RO_2\cdot \rightarrow R\cdot + O_2$ mechanism of this paper, one can account for the formation of these products by means of the mechanism shown in Chart V. This mechanism generates the triplet-spin O_2 ground state, and it is therefore consistent with the failure to observe any singlet O_2 chemiluminescence in these reactions.

Chart V



On the basis of these simple valence considerations, and in the absence of definitive structural data for the pernitrate ion, we conclude that the compound with the molecular formula $C_2H_3NO_5$ is better formulated as PAN rather than APN. Similar considerations also suggest that the PAN formulation should be preferred to those for three cyclic isomers, each having a 5-atom NO_4 ring.

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Received for review March 26, 1973. Accepted January 25, 1974.

Clean Environment for Ultratrace Analysis

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■ The inability to control ambient air blanks at levels insignificant in comparison with the constituent being determined severely restricts accuracy and precision of ultratrace metal determinations. Techniques are presented for upgrading a laboratory to control contamination from particulates in air. The importance of humidity control in eliminating electrostatic charges is discussed.

Determinations of trace (1–100 μg/g) and ultratrace (<1 μg/g) concentrations of metals in the human body are now assuming increasing importance in assessing exposure to toxic substances and in relating enhanced concentrations of these elements to arteriosclerosis, diabetes, and neoplastic disease. In the determination of chromium and nickel normally present in blood serum at 30 and 25 ng/g, respectively (*1*), the blank contribution of these elements from the laboratory atmosphere, as well as the chemical reagents and apparatus required for the analysis, may exceed that in the sample. This paper is concerned with the reduction in that portion of the blank contributed by laboratory air.

The effectiveness of our techniques in upgrading the air environment of a laboratory was demonstrated by the analysis of sodium carbonate samples prepared under a variety of conditions (Table I). Here an ultrapure solution of sodium carbonate was the starting point for all experiments. When this solution was converted to anhydrous sodium carbonate in a conventional laboratory, the iron content usually increased by a factor of 3–10. Iron continued to be the dominant trace transition element impurity even after all operations were carried out under class 100 clean conditions (*2*). This is not surprising since iron is the second most common metal (aluminum is first) on the earth's surface. The chromium and nickel content of the material prepared in the open laboratory was most surprising. The data suggest that the chromium and nickel content of our general laboratory environment can, indeed, play a significant role in determinations of these elements at the low ng/g level.

In current manual and automated methods of clinical analysis, the goals for relative standard deviation vary from 0.5–3%. Blood serum, for example, contains approximately 100 μg/g of calcium. The goal for the determination of calcium, however, is a precision of ± 0.5 μg/g (*3*). An error of 500 ng/g represents 20 times the normal nickel levels in blood serum. The relative standard deviation of 17 consecutive daily determinations of nickel in a pooled specimen of human serum has been reported to be ± 9.9% (*4*). Although it is not surprising that the standard deviation is an order of magnitude higher than that encountered in the calcium determination, complications during precise measurement of this element in blood due to atmospheric concentrations of nickel are not often recognized.

As much as 200 μg of dust/m³ is present in the unfiltered air of a noncontrolled laboratory (*5*). Analysis of such a sample showed that it contained 3% Fe and 1.5% Ni. Inasmuch as vanadium and nickel concentrations exceed 100 ng/m³ in the atmosphere of urban centers, contamination from ambient air influences blanks in precise ultratrace analysis of these elements (*6, 7*). The fallout of cadmium from the air in a conventional laboratory has been shown to make a significant contribution to the blank (*8*). Thus, blood and other samples must be handled in an environment meeting the class 100 cleanliness level under Federal Standard 209a for ultratrace results to be valid (*2*). Some hospitals send samples to a commercial or special regional laboratory for ultratrace analysis (*9*), but contamination during packaging of these samples in a conventional laboratory and subsequent shipment may well vitiate the results (*10*).

In the 1960's, the high cost of class 100 laminar flow clean rooms discouraged many applications. Today, existing laboratories can be upgraded with minimum alterations and with no loss in existing bench and floor space (*11*). To achieve an effective and economical conversion of a laboratory to class 100 conditions we have adopted a two-phase procedure in our laboratory to reduce high blanks in ultratrace analysis of diverse chemicals.

In Phase I the general laboratory space is given attention. All incoming air from air conditioning, heating, and ventilating sources must be provided with high-efficiency (85–95%) filters. All walls and ceilings should be coated with a nonshedding enamel paint. Floors should be covered with a vinyl floor covering. All unnecessary shelving, partitions, and furniture should be removed. All windows and wall openings must be made airtight by caulking to prevent dust penetration. In addition, the room must be kept under constant positive air pressure of at least 1.5 mm of mercury above ambient. To eliminate chemical vapors in the atmosphere, a ventilating unit containing an activated charcoal filter can be placed strategically in the laboratory.

Phase II is intended to supply clean air to critical work areas. Clean air modules (Microvoid IV M, 1.5 m wide × 0.76 m deep, Air Control Inc., Norristown, Pa.) are placed about 1 meter above laboratory bench tops (*11*). Figures 1 and 2 show the air flow pattern immediately after passing through a 70.3% dust-arrest prefilter. The air is then

Table I. Trace Impurities in Sodium Carbonate[a]

Sample	Cr	Cu	Fe	Ni
	Ng/g			
A[b]	<7	10	10	<10
B[c]	4	12	20	10
C[d]	37	24	80	29

[a] By DC-arc spectrography after collection via coprecipitation with indium using 8-quinolinol-tannic acid-thionalide and ignition to oxides against commercial standards in indium oxide (see R. L. Mitchell and R. O. Scott, Spectrochim. Acta, *31*, 367 (1948); E. F. Joy, N. A. Kershner and A. J. Barnard, Jr., *Spex Speaker*, 16(3),1 (1971).

[b] 25% Aqueous solution of sodium carbonate after mercury cathode electrolysis and filtration through a 0.2-μm cellulose acetate membrane filter in an all-Teflon housing; analysis based on sodium carbonate content.

[c] Anhydrous sodium carbonate obtained from sample A *in a class 100 laminar-flow hood*. The solution was frozen in a polyethylene table-top filter containing a 60-μm polyethylene frit. As the solid was allowed to reach room temperature slowly, a vacuum was applied to the filter. The moist solid was then dried in Teflon® TFE dishes at 185°C under a filtered argon blanket in a quartz-tube furnace.

[d] Same as 3 but sample A was worked up in the open laboratory without regard to a clean air environment.

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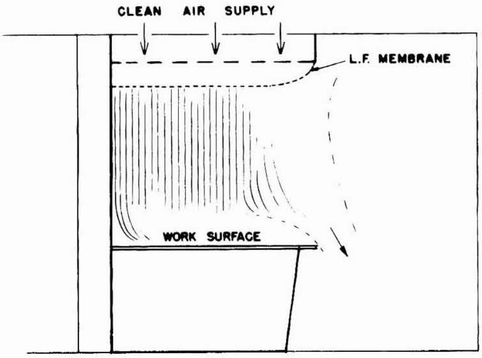

Figure 1. Vertical laminar flow unit with front diverging air flow for wall bench

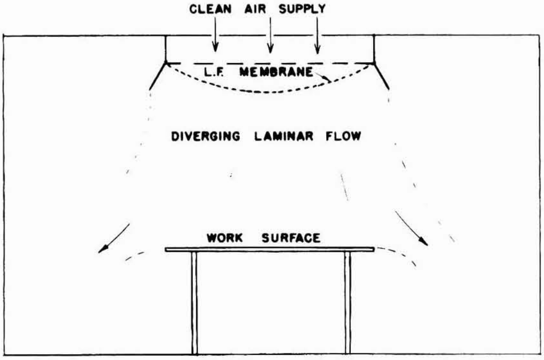

Figure 2. Diverging vertical laminar flow for center bench with access from both sides

forced by a blower system through a HEPA (high-efficiency particulate air) filter 99.97% efficient in removing particles of 0.5-μm diameter or greater. The clean air is then passed through a divergent anodized aluminum membrane containing holes (1.2 mm in diameter) spaced along the entire membrane at 4.8-mm intervals. The divergence of the membrane at the front of the laminar flow hoods gives the air flow patterns in Figures 1 and 2 made visible by holding a container of liquid nitrogen close to the anodized membrane. The sides and back of the hood beneath the membrane are constructed from 6.4-mm polypropylene panels.

The laminar flow membranes in these wall and center bench assemblies substantially eliminate the induction effects observed when front shielding panels are removed from conventional clean benches. Directional air thus provides an air curtain with unrestricted access for processing biological fluids and tissues.

The lower back portion of the clean hood should contain a louvered exhaust opening for venting noxious fumes. During all wet ashing the louvers should be positioned so that the air pattern of Figure 1 is maintained. Apparatus for fuming should be placed at the rear of the hood as close to the exhaust opening as possible to trap all vapors. In addition, the air flow speed should approximate 30 ± 3 m/min. At speeds below 18 m/min, fuming with acid over a six-month period can corrode the aluminum separators used to pleat the porous sheets of glass fiber filters in the HEPA filter and, thereby, ruin the integrity of the clean hood. On this account HEPA filters containing plastic separators are recommended for fuming. The anodized aluminum membranes are impervious to corrosion by fumes.

When Phases I and II are completed, the clean space under the HEPA filters fits the definition of a class 100 area; the rest of the laboratory becomes better than class 10,000. The relative humidity of the latter area must be kept between 45–50%. At lower relative humidity, airborne particles develop electrostatic charges that permit the particles to attach themselves to the technologist. These particles are rapidly transferred to the clean area when plastic apparatus is employed. For example, polyfluorohydrocarbons acquire negative charges readily during handling. Such transfer is also minimized when the technologist wears polyvinyl chloride gloves, lint-free hats and uniforms (nylon or Dacron) to prevent air travel of particles from clothing, skin, or hair. In addition to these precautions, laboratory walls and work areas should be vacuumed regularly; floors particularly need frequent cleaning to avoid airborne contamination. It is not enough to control one source of airborne contamination; all recognized sources must be monitored and certain clean room disciplines must be observed at all times.

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Received for review October 23, 1973. Accepted April 10, 1974.

CORRESPONDENCE

Air Quality Control Using Minimum Pollution Dispatching Algorithm

Sir: The paper summarizing the ongoing research by the authors [R. L. Sullivan and D. F. Hackett, *Environ. Sci. Technol.*, **17** (11), 1019–22 (1973)] is an interesting and timely contribution to an important problem, and we merely wish to add some additional concepts and ideas which extend the usefulness of their models. Particularly, we would like to elaborate on the authors' closing statements, that minimization techniques other than those presented should be considered.

To begin with, we wish to use a somewhat simpler notation as follows: Let there be J sources of power, $j = 1, 2, 3, \ldots, J$, and I receptor or control points, $i = 1, 2, 3, \ldots, I$. Let a_{ij} = ground level concentration of a pollutant at a point i from a unit of production at source j. Furthermore, let the production at point j be limited by lower and upper bounds—i.e., for all j, $l_j \leq P_j \leq u_j$, and let the SO_2 emission be related to power production by the function, $Q_j = \alpha_j + \beta_j P_j + \gamma_j P_j^2$, and let the total power requirement be P.

1. Consider now the case where we wish to minimize the ground level concentration for a particular point, say point 1. [The authors' terminology of "environmental cost" is somewhat awkward and inappropriate; their objective function (*1*) is the ground level concentration at a specific control point.] The mathematical programming problem then is,

$$\text{Minimize: } \sum_{j=1}^{J} a_{ij}(\alpha_j + \beta_j P_j + \gamma_j P_j^2)$$

$$\text{Subject to: } l_j \leq P_j \leq u_j \qquad j = 1, 2, 3, \ldots, J$$

$$\sum_{j=1}^{J} P_j \leq P$$

This type of problem is known as the quadratic programming problem—that is, to find the minimum of a quadratic function subject to linear constraints. There are several algorithms and computer programs available to solve this type of problem (*1, 2*). These algorithms have great advantages over the Lagrangian multiplier approach. While a Lagrangian multiplier approach and the Kuhn-Tucker condition identify a global optimum, they are not a readily implementable procedure to find the optimal solution. For a discussion of the problems with this approach, see Charnes and Cooper (*3*). To find a global optimum, the only requirement is that the function must be convex, which is the case here, since the function is a positive semidefinite quadratic form.

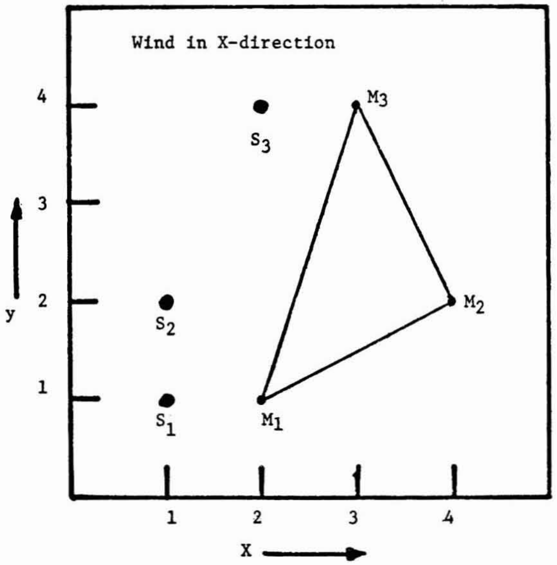

Figure 1. Three point sources of pollution

2. Consider now the case where one wishes to minimize the cost of producing power subject to the constraint that the ground level concentration at a particular point, say k, must be below some limiting value. Assume that the cost of producing power is a convex function of the form $f_j(P_j)$, then we have the problem,

$$\text{Minimize: } \Sigma f_j(P_j)$$

$$\text{Subject to: } l_j \leq P_j \leq u_j$$

$$\sum_{j=1}^{J} P_j \geq P$$

$$\sum_{j=1}^{J} a_{kj}(\alpha_j + \beta_j P_j + \gamma_j P_j) \leq C_k$$

Again, this is a convex programming problem with one additional quadratic constraint. But, it is a convex constraint, and can be handled by the penalty function approach by adding the constraint to the objective function.

3. Consider now the case where the maximum allowable ground level concentration is specified not for a single control point, but for an entire area. The basic problem then is to determine where to locate the, for example, control points, such that these points will be representing the areas of maximum concentration. One approach is to put a fine grid over the area of interest, and specify a maximum ground level concentration for every point, This, of course, leads to a large number of constraints and a significant computational burden. A more efficient approach is to exploit the properties of the dispersion model equation. This function is a unimodal function reaching its maximum value at a certain distance downwind from the source. The ground level concentration of any point is the summation of the contributions from each source, and this function is a multipeak surface obtained by summing the individual unimodal functions. It is not known, a priori, which of the peaks is the greatest, nor where the peaks actually occur. However, since all the individual functions are of the unimodal type, the maxima (peaks) must occur on a line connecting the maxima of the individual functions. It is therefore sufficient to write the constraints for a number of points along these lines. If the constraints are met at these points, they will be met at every other point in the region (*4*).

Consider, for example, three sources of pollution, arranged in an area as shown in Figure 1. Assume a wind direction that is out of the west (in X direction), and further assume for simplicity the dispersion model to be of the form

$$C_1(x,y) = [1/(x-1)]\, e^{-1/(x-1)[1+(y-1)^2]}$$

$$C_2(x,y) = [1/(x-1)]\, e^{-1/(x-1)[3+(y-3)^2]}$$

$$C_3(x,y) = [1/(x-2)]\, e^{-1/(x-2)[2+(y-4)^2]}$$

The individual maximum ground level concentrations of the three sources will occur at the points M_1, M_2, and M_3. It is therefore sufficient to write the constraints for the ground level concentrations at points along the lines connecting these three points.

Finally, we wish to point out that the authors might want to consider the operation of the generators at the power stations as an on-off proposition—that is, a generator is either operating or not. Under this assumption, the problems may be reformulated as integer programming problems.

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Sir: The authors (R. L. Sullivan and D. F. Hackett) would like to thank Deininger and Cohen (see above) for their interesting response to the authors' paper on ambient air quality control [*Environ. Sci. Technol.*, **17** (11), 1019–221 (1973)]. Since they made several points concerning various aspects of the paper, each point will be addressed separately.

As Deininger and Cohen correctly pointed out, the basic problem could be formulated as a quadratic programming problem subject to either linear or quadratic constraints, where solution techniques for solving such problems are readily available. The Lagrange multiplier and Kuhn-Tucker approach was used in the paper in spite of the computational difficulties, which can be circumvented (*1*), because of the inherent valuable control information associated with the various multipliers.

For the power system dispatcher to make a control decision, it is often convenient and necessary to have sensitivity information for each of the independent parameters. The Lagrange multiplier, λ, for example, provides the dispatcher with sensitivity information relating the change in ground level concentrations to the change in the amount of imported or exported power (*2*)—i.e.,

$\lambda = -\dfrac{\Delta L}{\Delta P_T}$ or specifically

$$\lambda = -\frac{P_{\text{Load}} + P_T + \sum_{i=1}^{G} \dfrac{\beta_i}{\gamma_i}}{\sum_i \dfrac{1}{M_i K_i \gamma_i}} \tag{1}$$

$$L = \sum_{i=1}^{G} \epsilon_i = \sum_{i=1}^{G} M_i Q_i = \sum_i^{G} M_i k_i \left(\alpha_i + \beta_i P_{Gi} + \frac{\gamma_i}{2} P_{Gi}{}^2\right)$$

$$P_T = \Sigma P_{Gi} - P_{\text{Load}}$$

L = ground level SO_2 concentration in ppm
M_i = meteorological coefficient containing all meteorological parameters
k_i = conversion factor converting quadratic cost curves into quadratic emission rate curves

From Equation 1, we have

$$\Delta L = -\lambda\ \Delta P_T \text{ or } \Delta P_T = -\frac{\Delta L}{\lambda}$$

With this information and incremental cost information for the two systems involved, and operator could determine the cost of decreasing the ground level concentration by amount ΔL. Obviously, it is also possible to utilize the Kuhn-Tucker dual variables in the same manner.

Another advantage of the approach taken by the authors is that if no inequality constraints are violated, then an optimal linear control law defined by the following equation can be developed:

$$\Delta \begin{vmatrix} P_{G1} \\ \vdots \\ P_{GG} \end{vmatrix} = K \begin{vmatrix} \Delta P_{L1} \\ \vdots \\ \Delta P_{LN} \end{vmatrix} \tag{2}$$

ΔP_{Gi} = change in output of generator i
ΔP_{Lj} = change in load at bus j

The optimal control strategy defined by Equation 2 facilitates changing the generator outputs automatically as *small* changes in load occurs, thus ensuring continuous minimum pollution dispatching (*1*).

Deininger and Cohen also suggest a problem formulation that is amenable to integer programming techniques. Unfortunately the authors feel that the use of integer programming is inappropriate in this case since the requirement that the generators must be on or off is implied. In reality, generators operate, once they are on-line, over their complete capability range in a continuous fashion, although certainly the range of operation could be discretized to allow only integer operating levels. Integer programming could be used, however, to determine which generators to commit to service, since in this case the generators are either committed or not committed—a point worth further investigation.

To conclude this discussion, the authors would like to point out that this basic approach to ambient air quality control should be classified as an on-line approach only. It does not, for example, suggest how a given utility with a certain amount of low-sulfur fuel could best utilize that fuel, taking into consideration generator forced outages and maintenance schedules. The authors are presently investigating a technique that is basically a probabilistic planning tool for determining minimum pollution fuel usage strategies and maintenance schedules.

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CURRENT RESEARCH

Effects of gasoline aromatic and lead content on exhaust hydrocarbon reactivity 641

J. M. Heuss,* G. J. Nebel, and B. A. D'Alleva

Effects of lead and aromatic hydrocarbons in gasoline were studied for activity relating to eye irritation and ozone or NO_2 formation. Lead did not affect exhaust reactivity, but aromatics increased reactivity criteria associated with eye irritation.

Characteristics of laminar jet impactors 648

V. A. Marple and B. Y. H. Liu*

Theoretical characterization of jet impactors was done by the numerical solution of the Navier-Stokes equation. This theoretical study was verified by comparison with experimentally determined impact points. Effects of jet-to-plate distance, jet Reynolds number, and jet throat length are discussed.

Solubility of higher-molecular-weight *n*-paraffins in distilled water and seawater 654

Chris Sutton and J. A. Calder*

Solubilities of several *n*-paraffins were found to be less in seawater than in distilled water. The magnitude of the salting out is in accordance with the McDevitt-Long theory. Calculations using this theory gave salt coefficients in agreement with those obtained experimentally.

Oceanic distribution of low-molecular-weight hydrocarbons. Baseline measurements 657

J. W. Swinnerton and R. A. Lamontagne

Surface water samples were collected from many ocean areas and analyzed for light hydrocarbons by gas chromatography. An empirical relationship, the Contamination Index, is proposed to differentiate between clean and contaminated ocean water.

Bacterial degradation and emulsification of No. 6 fuel oil 664

J. E. Zajic,* Bernard Supplisson, and Bohumil Volesky

Bacterial cultures isolated from sewage synthesize an active emulsifying agent from the paraffinic components of No. 6 fuel oil. The emulsifier appears to be a large polysaccharide, and the emulsification process is inhibited by low temperatures and high salt levels.

Monitoring Narragansett Bay oil spills by infrared spectroscopy 669

C. W. Brown,* P. F. Lynch, and Mark Ahmadjian

An oil spill was monitored by infrared spectroscopy for 30 days. All the samples collected during this period could be traced to the source of the spill by their ir spectra. Two subsequent slicks in the area were shown to be from a different source by the same method.

NOTES

Cryogenic separation of methane from other hydrocarbons in air 671

J. C. Cooper,* H. E. Birdseye, and R. J. Donnelly

Since methane has a higher vapor pressure than other hydrocarbons, it can be separated by condensing the heavier ones on a suitably cold surface. A methane separator has been built and tested to trap 95% of all nonmethane hydrocarbons.

Algal blooms—possible effects of iron 673

S. D. Morton* and T. H. Lee

Increases in total iron cause a shift in the dominant type of algae grown in cultures from greens to blue-greens. Results were not dependent on manganese or phosphorus concentrations.

Valence formula for $C_2H_3NO_5$—PAN or APN? 675

R. D. Harcourt* and D. P. Kelly

The compound with the formula $C_2H_3NO_5$, formed in the reactions of auto exhaust with oxygen or ozone, because of valence considerations, is better formulated as peroxyacetylnitrate (PAN) than as acetylpernitrate (APN).

Clean environment for ultratrace analysis 677

Morris Zief* and A. G. Nesher

Metals in particulates in ambient laboratory air restrict precision and accuracy in ultratrace metal determinations. Methods for increasing laboratory control of these contaminants are presented. The importance of humidity control is also discussed.

CORRESPONDENCE

Air Quality Control Using Minimum Pollution Dispatching Algorithm 679

R. A. Deininger* and J. M. Cohen
R. L. Sullivan

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* To whom correspondence should be addressed.

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

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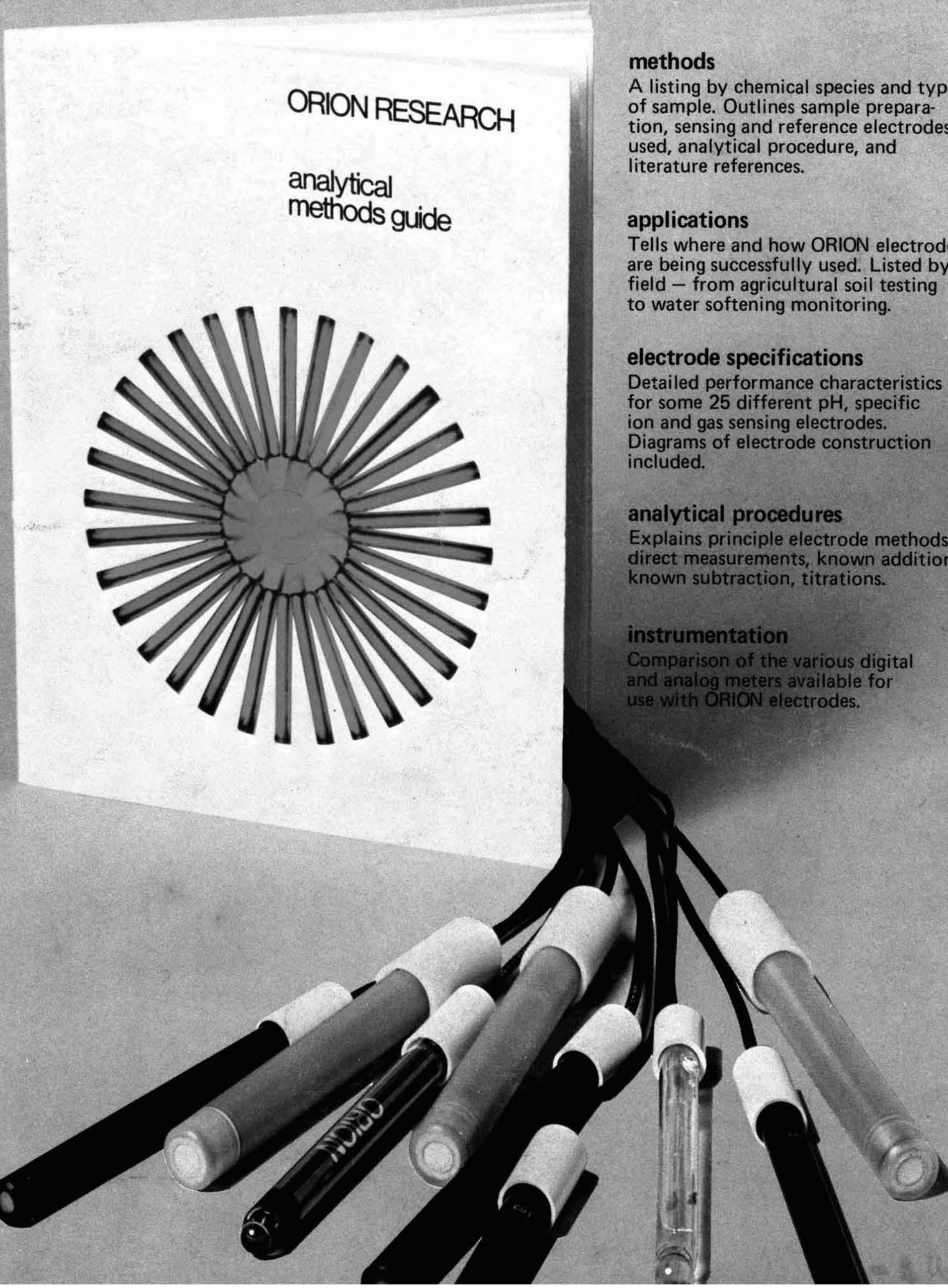
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